DYNAMICS OF POINT DEFECTS
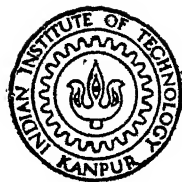
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DYNAMICS OF POINT DEFECTS

A Thesis Submitted
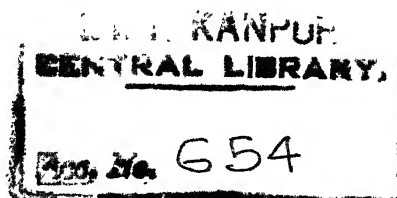
In Partial Fulfilment of the Requirements

for the Degree of

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by

MANOJ SACHDEV

to the

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INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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Certified that the work 'Dynamics of Point Defects'
has been carried out by Miss Manoj Sachdev under my
supervision and the same has not been submitted elsewhere
for a degree.

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ABSTRACT

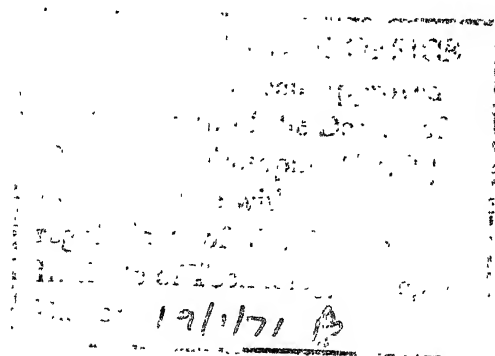This thesis contains some results of model calculations on the dynamics of point defects using a pseudomolecular model. Chapter I contains a discussion of the pseudomolecular model in which a defect can be treated as a pseudomolecule embedded in the rest of the crystal. The pseudomolecular frequencies can be defined in terms of the effective force constants obtainable in terms of the zero frequency limit of the molecular Green functions. The self-entropy of a general point defect can be expressed as a function of the perturbed and unperturbed pseudomolecular frequencies by choosing the pseudomolecule such that the force constants between its boundary atoms and atoms of the unperturbed region remain unchanged. The expressions for self-entropy of substitutional defects and vacancies in some lattice models are given in Chapter III.

In Chapter IV, a formalism for studying the time-dependent dynamics of point defects in terms of the spectral density matrices derivable from the molecular Green functions (for non-zero frequencies) has been given. The time-asymptotic form of a normal mode can be studied in terms of the isolated singularities and critical points of the spectral density functions. A sum rule for the spectral density matrices of the perfect pseudomolecules has been given.

Neglecting relaxation of the medium around the vacancy,
it has been shown that a vacancy in the simple cubic lattice
does not have localized modes of vibration. A method of
obtaining correlation functions of a point defect has been
discussed. This method has been used to obtain an expres-
sion for the Debye-Waller factor of one of the nearest neighbours
of a vacancy in the simple cubic lattice.

For lattices with polarisable atoms a modified pseudo-
molecular model in terms of the core and shell co-ordinates
has to be used. Such a model has been discussed in Chapter
V. It has been illustrated for a substitutional defect
which does not change the long-range Coulomb interactions
in the simple cubic lattice.

CHAPTER I

INTRODUCTION

The theory for investigation of the dynamical proper-
ties of imperfect crystals was given by Lifshitz[1,2] in
connection with the optical properties of non-ideal cryst-
als in the infra-red region. A similar method was later
developed independently by Montroll and Potts[3]. Since at
non-zero temperatures every substance contains a finite
concentration of defects which play an important role in
many physical properties like optical absorption, thermal
conductivity, diffusion etc., the theoretical and experi-
mental aspects of this problem were studied subsequently
by many authors. The subject has been reviewed exhaustively
in two recent articles by Maradudin[4,5].

The earlier techniques used in this problem exploit
the fact that a local perturbation on the masses and force
constants due to a defect can be represented by a perturb-
ation matrix having a dimension much smaller than that of the full
dynamical matrix of the perfect crystal. This enables a
Green function method to be adopted for the evaluation of
the perturbed eigenvectors and eigenfrequencies, in which
the secular equation for the perturbed frequencies can be
written in terms of a subspace, the coordinate indices of
which refer to those of the affected atoms. Such an approach is
applicable only to impurities which do not change the number of
degrees of freedom associated with the perfect crystal.
Stripp and Kirkwood[6] have used perturbation theory for

A logical extension of the previous methods is to treat the defect region as a pseudomolecule which is embedded in the host crystal, and which interacts with the latter. This approach is possible through a partitioning technique which enables one to write the explicit equations of motion of the atoms in the defect region including its coupling to the rest of the crystal. This method has been used by many workers[7,8,9] in connection with different aspects of imperfect lattices. The effective interaction of the pseudomolecule with the host lattice can be evaluated exactly, for short range inter- actions, in terms of the Green functions and lattice parameters. In this thesis, the results of lattice dynamical studies of point defects on the basis of the pseudomolecular model will be presented.

As an illustration of the use of this approach to the study of crystal defect problems mention may be made of computation of the vibrational self-entropy[10] of a point defect. The self-entropy of a point defect at high temper- atures is expressible as a function of the ratio of the pert- urbed and unperturbed frequencies[11,12]. As this problem reduces essentially to determining the perturbed spectrum, the previous exact methods for determining the self-entropy[13,14] are based on the Green function method or perturbation method. Among the approximation methods, Huntington et al.[11] have used the Einstein model for finding the perturbed frequencies of atoms in the vicinity of defect. They have calculated the contributions to the self-entropy from the region of elastic

strain and surface effects separately. Theimer[15] and Chandra
etal[16] have assumed the changes in frequencies due to the defect to be small
for finding the entropy of formation of a vacancy in the ionic
crystals. Matthew[17] has discussed the relative limitations
of these approximation methods. Using the pseudomolecular
model, the self-entropy of a point defect can be obtained
from the ratio of the products of frequencies of the perfect
and imperfect pseudomolecules[10]. This method is physically
more realistic as the exact interaction of impurity with the
host lattice is taken into account. Furthermore, the pseudo-
molecular method has the advantage of being applicable to
a general point defect which may involve a change in the
number of degrees of freedom of the lattice. Computationally,
also, this method is not more involved than the conventional
methods[13,14] as the secular determinants of the pseudomole-
cules can be block-diagonalised by using the point symmetry
of the lattice. In the present model calculations we have
obtained the pseudomolecular frequencies for substitutional
impurities and vacancies in the square, simple cubic and
B.C.C. lattices.

The pseudomolecular method is also useful for the study
of detailed dynamics of point defects, a knowledge of which
is required for studying physical properties like optical
absorption and Mössbauer line-width etc.[4,5]. This method
enables the exact dynamics of impurity to be studied in terms
of the spectral density functions of the normal modes of
vibration of the defect pseudomolecule. The spectral density

functions are quite complicated, in general, and therefore the integrals required for obtaining the explicit time-dependence of the atomic displacements are difficult to evaluate even for isotope defects in the linear lattices. However, a knowledge of the time-asymptotic-behaviour of the displacements, which is governed by the nature of spectral density functions at the critical points and singularities, can be used to investigate the possibilities of occurrence of persistent modes of vibration. Relaxing modes of vibration correspond to the well-behaved part and persistent modes to the isolated singularities of the spectral density functions. The present method shows exactly that a vacancy in the simple cubic lattice (relaxation around the vacancy has not been taken into account) does not have localized modes of vibration, a result which was proved earlier by Lengeler and Ludwig[18] by an approximation method. A formalism for computing the correlation functions of a general point defect by the pseudo-molecular model has also been given.

For a lattice with polarisable atoms, Page and Strauch[19] have given a perturbation method based on Lifshitz's Green function method for studying the dynamics of an impurity which does not change the long-range Coulomb terms. A pseudo-molecular model for such a case has been discussed in Chapter V of the present work.

CHAPTER II

A PSEUDOMOLECULAR MODEL

2.1 Partitioning Technique

The dynamical equations of atoms belonging to a certain subspace of a crystal can be separated by partitioning various matrices occurring in the equations of motion of the entire crystal. The procedure is similar to what has been used by Löwdin[20] for contraction of secular equations in connection with quantum-chemical problems. Löwdin has shown that a secular equation in a certain representation can be contracted to a similar secular equation of smaller degree and referring to a subspace of the original basis by partitioning the matrices suitably. The contracted secular equation so obtained contains energy as a non-linear parameter. Inspite of the simple nature of the original secular equation, solution of the contracted secular equation by iteration procedures is more accurate, as has been pointed out by Löwdin[21]. Also, the solution of the contracted secular equation by Newton-Raphson's second order iteration method assumes a very simple form which shows its analogy with the variation method and connection with the general perturbation technique.

The equation of motion of a perfect lattice having N degrees of freedom can be written in matrix notation as,

$$\hat{M} \, \underset{\sim}{\ddot{X}}(t) = \hat{L} \, \underset{\sim}{X}(t) \, , \qquad (2.1)$$

where $\hat{L}$ is a (NXN) matrix of atomic force constants, $\hat{M}$ is a N-dimensional diagonal matrix of atomic masses and $\underline{X}(t)$ is a N-dimensional vector having time-dependent atomic displacements as its components.

Assuming $\underline{X}(t) = e^{i\omega t} \underline{U}(\omega)$ in equation (2.1), the following time-independent equation of motion of the lattice is obtained,

$$(\hat{L} - \hat{M}\omega^2)\ \underline{U}(\omega) = 0 \qquad (2.2)$$

We partition the matrices $\hat{L}$, $\hat{M}$ and vector $\underline{U}(\omega)$ in eqn. (2.2) as follows,

$$\hat{L} = \begin{pmatrix} \hat{A} & \hat{B} \\ \hat{B}^T & \hat{C} \end{pmatrix}$$

$$\hat{M} = \begin{pmatrix} \hat{M}_A & 0 \\ 0 & \hat{m} \end{pmatrix} \qquad\qquad \underline{U} = \begin{pmatrix} \underline{U}_1(\omega) \\ \underline{U}_2(\omega) \end{pmatrix} \qquad (2.3)$$

where matrices $\hat{C}$, $\hat{m}$ and vector $\underline{U}_2(\omega)$ refer to a region Γ_2 of the perfect crystal which will subsequently be perturbed by a point defect. The corresponding matrices for the imperfect crystal shall be denoted by $\hat{L}'$, $\hat{M}'$ and $\underline{U}'$, respectively. The partitioned forms of these perturbed matrices shall be similar to those given by eqns. (2.3) with all the submatrices, except $\hat{A}$ and $\hat{M}_A$, as primed. $\hat{A}$, $\hat{M}_A$ and $\underline{U}_1(\omega)$ refer to the unperturbed part Γ_1 of the crystal. $\hat{B}$ and $\hat{B}^T$ are matrices of the force constants between the atoms of regions Γ_1 and Γ_2. We assume that the region Γ_2

has n and n' degrees of freedom associated with it for the perfect and imperfect crystals, respectively.

Using eqns. (2.3) in eqn. (2.2) we get the following two sets of N-n and n equations in matrix notation,

$$(\hat{A}-\hat{M}_A\omega^2)\underline{U}_1+\hat{B}\underline{U}_2 = 0 \qquad (2.4)$$

$$\hat{B}^T\underline{U}_1+(\hat{C}-\hat{m}\omega^2)\underline{U}_2 = 0 \qquad (2.5)$$

From eqns. (2.4) and (2.5), the equations for $\underline{U}_1$ and $\underline{U}_2$ referring to the regions Γ_1 and Γ_2, respectively, can be separated as,

$$(\hat{A}-\hat{M}_A\omega^2-\hat{B}(\hat{C}-\hat{m}\omega^2)^{-1}\hat{B}^T)\underline{U}_1 = 0 \qquad (2.6)$$

$$(\hat{C}-\hat{m}\omega^2-\hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B})\,\underline{U}_2 = 0 \qquad (2.7)$$

2.2 The Pseudomolecular Model for a Point Defect

A pseudomolecular model for a point defect can be given from the contracted equation (2.7). Eqn. (2.7) can be interpreted as the equation of motion of a pseudomolecule having n degrees of freedom and embedded in the rest of the crystal having (N-n) degrees of freedom. Comparing eqn. (2.7) with the original equation of motion viz., eqn. (2.2), the additional term $\hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}$ here can be assumed to represent an effective interaction of the pseudomolecule with the rest of the lattice. This type of approach has been used by many authors[7-9] for various lattice-dynamical problems.

Litzman and Rozsa[7] have calculated the frequencies of localized modes of a defect in the square lattice by taking a pseudomolecule of thirteen atoms. They have partitioned the total space into three subspaces. Explicit evaluation of $\hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}$ matrix, as has been mentioned by Litzman and Rozsa, is an extremely difficult task except for the case of a linear lattice. However, by using certain identities satisfied by the submatrices of the matrix $(\hat{L}-\hat{M}\omega^2)$ and its inverse $(\hat{L}-\hat{M}\omega^2)^{-1}$, it can be written in terms of the known matrices.

By partitioning the matrices $(\hat{L}-\hat{M}\omega^2)$ and $(\hat{L}-\hat{M}\omega^2)^{-1}$ as shown below

$$(\hat{L}-\hat{M}\omega^2) = \begin{pmatrix} \hat{A}-\hat{M}_A\omega^2 & \hat{B} \\ \hat{B}^T & \hat{C}-\hat{m}\omega^2 \end{pmatrix} ;$$

$$(2.8)$$

$$(\hat{L}-\hat{M}\omega^2)^{-1} = \begin{pmatrix} \hat{G}_A(\omega) & \hat{G}_B(\omega) \\ \hat{G}_B^T(\omega) & \hat{G}_C(\omega) \end{pmatrix} ,$$

it can be proved[7],

$$\hat{G}_C^{-1}(\omega) = \hat{C}-\hat{m}\omega^2 - \hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}. \qquad (2.9)$$

Substituting eqn. (2.9) in eqn. (2.7), the dynamical equation of the pseudomolecule can be written as

$$\hat{G}_C^{-1}(\omega)\underline{U}_2(\omega) = 0 \qquad (2.10)$$

By using the notation explained for eqn. (2.3), the dynamical equation for the imperfect pseudomolecule can similarly be written by priming the various submatrices occurring in eqn. (2.7) as,

$$(\hat{C}'-\hat{m}'\,\omega^2-\hat{B}'^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\hat{B}'))\underline{U}'_2(\omega) = 0. \qquad (2.11)$$

To evaluate $\hat{B}'^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\hat{B}'$ matrix in eqn. (2.11), we use the following property of this matrix. A typical element $(\ell\ell')$ of the matrix $\hat{B}^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\hat{B}$ is given by,

$$\left[\hat{B}^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\hat{B}\right]_{\ell\ell'} = \sum_{R,R'} \hat{B}^T(\ell,R)\,(\hat{A}-\hat{M}_A\,\omega^2)^{-1}_{R,R'}\,\hat{B}(R;\ell'). \qquad (2.12)$$

In eqn. (2.12), ℓ and ℓ' refer to the indices of the pseudo-molecule and R and R' refer to those of the unperturbed subspace Γ_1. If the force constant between an ℓ atom and a R atom is denoted by $\gamma_{\ell R}$, eqn. (2.12) can be written as

$$\left[\hat{B}^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\hat{B}\right]_{\ell\ell'} = \sum_{\substack{\text{All the R}\\\text{atoms inter-}\\\text{acting with}\\\ell}} \sum_{\substack{\text{All the}\\\text{R' atoms}\\\text{interact-}\\\text{ing with } \ell'}} \gamma_{\ell R}\,\gamma_{\ell' R'}\,(\hat{A}-\hat{M}_A\,\omega^2)^{-1}_{RR'}$$

$$(2.13)$$

It follows from eqn. (2.13) that for defects which do not involve a change in the degrees of freedom asso-ciated with the crystal, $\hat{B}'^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\hat{B}'$ and $\hat{B}^T(\hat{A}-\hat{M}_A\,\omega^2)\hat{B}$ will be exactly identical if $\gamma_{\ell R}$'s do not change. For

short range interactions, this can always be done by
choosing the pseudomolecule in such a way that the subst-
ituted or removed atoms do not directly interact with the
atoms of the unperturbed region. But if the defect changes
the number of degrees of freedom of the crystal (i.e., $n' \neq n$),
$\hat{B}'^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}'$ and $\hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}B$ shall differ in
dimension . However, with the above-mentioned choice of
the pseudomolecule, these matrices will have exactly ident-
ical non-zero elements. Therefore $\hat{B}'^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}'$ can be
obtained from $\hat{B}^T(\hat{A}-\hat{M}\omega^2)^{-1}\hat{B}$ by addition (for $n' > n$) or by
deletion ($n' < n$) of rows and columns of zeros correspond-
ing to the indices of added or removed atoms, respectively.

$$\hat{B}'^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}' = \left[\hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}\right]_{c,a} , (2.15)$$

where $\left[\cdots\right]_{c,a}$ denotes contraction (or addition) for $n' < n$
(or $n' > n$), respectively.

It is possible to derive some useful relations between
the secular determinants of the perfect and imperfect
crystals.

The secular equation of the perfect crystal can be
written from eqn. (2.2) as,

$$\left|\hat{L}-\hat{M}\omega^2\right| = 0 \qquad (2.16)$$

By partitioning the matrices in eqn. (2.16) as shown by
eqn. (2.8) we get

$$\left| \hat{L} - \hat{M}\omega^2 \right| = \begin{vmatrix} \hat{A} - \hat{M}_A\omega^2 & \hat{B} \\ \hat{B}^T & \hat{C} - \hat{m}\omega^2 \end{vmatrix}$$

$$= \left| \begin{pmatrix} \hat{A} - \hat{M}_A\omega^2 & 0 \\ \hat{B}^T & \hat{C} - \hat{m}\omega^2 \end{pmatrix} + \begin{pmatrix} 0 & \hat{B} \\ 0 & 0 \end{pmatrix} \right|$$

$$= \left| \begin{pmatrix} \hat{A} - \hat{M}_A\omega^2 & 0 \\ \hat{B}^T & \hat{C} - \hat{m}\omega^2 \end{pmatrix} \left(\hat{I} + \begin{pmatrix} \hat{A} - \hat{M}_A\omega^2 & 0 \\ -(\hat{C} - \hat{m}\omega^2)^{-1}\hat{B}^T(\hat{A} - \hat{M}_A\omega^2)^{-1} & (\hat{C} - \hat{m}\omega^2)^{-1} \end{pmatrix} \times \right. \right.$$

$$\left. \left. \begin{pmatrix} 0 & \hat{B} \\ 0 & 0 \end{pmatrix} \right) \right|$$

$$= \left| \hat{A} - \hat{M}_A\omega^2 \right| \left| \hat{C} - \hat{m}\omega^2 \right| \left| \hat{I} - (\hat{C} - \hat{m}\omega^2)^{-1}\hat{B}^T(\hat{A} - \hat{M}_A\omega^2)^{-1}\hat{B} \right|$$

$$= 0. \tag{2.17}$$

Similarly, the secular equation for the imperfect crystal can be written as

$$\left| \hat{L}' - \hat{M}'\omega^2 \right| = \left| \hat{A} - \hat{M}_A\omega^2 \right| \left| \hat{C}' - \hat{m}'\omega^2 \right| \left| \hat{I} - (\hat{C}' - \hat{m}'\omega^2)^{-1}\hat{B}'^T(\hat{A} - \hat{M}_A\omega^2)^{-1}\hat{B}' \right| \tag{2.18}$$

From eqns. (2.17) and (2.18) we get

$$\frac{\left| \hat{L}' - \hat{M}'\omega^2 \right|}{\left| \hat{L} - \hat{M}\omega^2 \right|} = \frac{\left| \hat{C}' - \hat{m}'\omega^2 - \hat{B}'^T(\hat{A} - \hat{M}_A\omega^2)^{-1}\hat{B}' \right|}{\left| \hat{C} - \hat{m}\omega^2 - \hat{B}^T(\hat{A} - \hat{M}_A\omega^2)^{-1}\hat{B} \right|} \tag{2.19}$$

Eqn. (2.19) shows that the ratio of the secular determinants of the imperfect and perfect crystals is given by the ratio of the contracted secular determinants of the imperfect and perfect pseudomolecules. This result will be used in Chapter III to find the self-entropy of point defects.

2.3 Effective Interaction Matrix

The pseudomolecular method reduces the degree of the secular equation and facilitates inclusion of any changes in the number of degrees of freedom associated with the perfect region due to the impurity and it takes into account the exact interaction of the defect with the crystal. Equation of motion of the atoms belonging to regions Γ_1 and Γ_2 have been written down separately as eqns. (2.6) and (2.7), respectively. These equations are exact as the interaction between the atoms of Γ_1 and Γ_2 is taken into account by the effective interaction matrices $\hat{B}(\hat{C}-\hat{m}\,\omega^2)^{-1}\hat{B}^T$ and $\hat{B}^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\hat{B}$.

Some interesting results can be derived from the effective interaction matrices. By using approximate expansions of $(\hat{A}-\hat{M}_A\omega^2)^{-1}$, Krumhansl and Matthew[8] have obtained equations for determining the frequencies of very high-frequency localized modes and low-frequency resonances from the secular determinant of the impurity pseudomolecule. These equations have been claimed to be as accurate as some of the other numerically computed results based on some special choice of the force constants.

In the present work, we have not considered the scattering of lattice waves by general point defects. If the subspace $\underline{U}_1$ (§2.1) is defined such that it refers to the vices of unperturbed atoms and the three centre of mass dinates of an atom having the mass of the molecular

impurity, the resulting equation (2.6) will be the equation for a lattice having the same number of degrees of freedom as the perfect crystal and can then be solved by Lifshitz's method. Using this method, Wagner[9] has studied the scattering of phonons by molecular impurities. By eliminating the additional degrees of freedom due to the molecule, he has shown that the usual local perturbation matrix of the imperfect crystal contains an additional term having a form similar to $\hat{B}(\hat{C}-\hat{m}\,\omega^2)^{-1}\,\hat{B}^T$ which has poles at the molecular frequencies; $(\hat{C}-\hat{m}\,\omega^2)^{-1}$ being the molecular Green function matrix. Wagner has further shown that the t-matrix of the scattering formalism and, consequently, the scattering cross-section show sharp resonances near the molecular frequencies. A similar approach, regarding the defect as a particle embedded in the phonon field, has been given by Krumhansl[22] for studying the scattering of lattice vibrations by vacancy-type defects.

The matrices $\hat{B}^T(\hat{A}-\hat{M}_A\,\omega^2)^{-1}\,\hat{B}$ and $\hat{B}(\hat{C}-\hat{m}\,\omega^2)^{-1}\,\hat{B}^T$ can be computed in terms of the Green function submatrices $\widetilde{G}_C^{-1}$ and $\hat{G}_A^{-1}$ from eqn. (2.9). $\hat{G}_C^{-1}$ is not difficult to obtain as it has the point symmetry of the lattice and can therefore be block-diagonalised by using group-theoretical methods. In cases where group-theoretical methods of inverting matrices by block-diagonalisation become involved an alternative method suggested by Litzman[7] may be used. This method is based on a theorem which states that a unitary matrix

constructed from the known eigen vectors of any matrix
partially diagonalises all the matrices commuting with
that matrix.

The pseudomolecular model presented in this Chapter
has to be modified for lattices with long-range interactions
due to polarizable atoms. This will be discussed in detail
in Chapter V.

CHAPTER III

VIBRATIONAL SELF-ENTROPY OF POINT DEFECTS

§3.1 Introduction

The vibrational self-entropy of a point defect ΔS, defined as the thermal entropy of formation of the defect, in the harmonic approximation is given by[12],

$$\Delta S = S'-S$$

$$= -\sum_r k_B \left\{ \ln\left[1-\exp\left(-\frac{\hbar\omega'_r}{k_B T}\right)\right] + \left(\frac{\hbar\omega'_r}{T}\right)\left[\exp\left(\frac{\hbar\omega'_r}{k_B T}\right)-1\right]^{-1}\right\}$$

$$\tag{3.1}$$

$$+ \sum_i k_B \left\{ \ln\left[1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)\right] + \left(\frac{\hbar\omega_i}{T}\right)\left[\exp\left(\frac{\hbar\omega_i}{k_B T}\right)-1\right]^{-1}\right\}$$

where S',ω' and S,ω are the entropy and frequencies of the imperfect and perfect crystals, respectively. k_B is the Boltzmann's constant and T is the temperature of the crystal.

For high temperatures (i.e., $k_B T \gg \hbar\omega_D$), eqn.(3.1) reduces to

$$\Delta S \simeq -\frac{k_B}{2}\ln\left[\left(\frac{\hbar}{k_B T}\right)^{2(N'-N)}\left(\prod_{r=1}^{N'}\omega'_r{}^2 \Big/ \prod_{i=1}^{N}\omega_i^2\right)\right] + (N'-N)k_B,$$

$$\tag{3.2}$$

where N' and N are degrees of freedom associated with the imperfect and perfect crystals, respectively. In eqn.(3.2) terms of order $\gg \left(\frac{\hbar\omega_D}{k_B T}\right)^2$ have been neglected, ω_D being the Debye frequency.

From eqn. (3.2) it is clear that knowledge of the frequency-spectrum of the perturbed and unperturbed crystals is required for evaluation of ΔS. This problem has been studied in detail by many authors[1-6]. A series of exact calculations of ΔS for a mass defect in the simple cubic lattice, a vacancy in the f.c.c. lattice, substitutional defects in simple cubic lattices have been given, respectively, by Naradelli and Tettamanzi[13], Nardelli and Terzi[14] and Mahanty[23]. These calculations are all based on Lifshitz's Green functions method. It can be shown that for N'=N, ΔS is expressible as[23],

$$\Delta S = - \lim_{\omega \to 0} \frac{k_B}{2} \ln \Delta(\omega) \qquad (3.3)$$

where $\Delta(\omega) = \left| \hat{I} + \hat{G}\,\hat{P} \right|$ with $\hat{G}$ and $\hat{P}$ as the Green function and perturbation matrices of the perfect and imperfect crystals, respectively, is called the defect determinant. The perturbation matrix $\hat{P}$ has only a few non-vanishing elements which can be grouped together to form a submatrix $\hat{p}$ in a certain subspace Γ_2 of the crystal. Furthermore, the submatrices $\hat{p}$ and $\hat{g}$ have the point symmetry of the sub-space Γ_2. This feature can be exploited to block-diagonalise $\Delta(\omega)$ by group-theoretical methods which enable one to determine the contributions to ΔS, from the modes belonging to various irreducible representations of the point symmetry group of Γ_2. We have given the block-diagonalised form of $\Delta(\omega)$ for a substitutional impurity

in the simple cubic lattice in Appendix I. Benedek and
Nardelli[24] have expressed ΔS in terms of the numerator
and resonance-denominator $(\equiv \Delta(\omega))$ of the scattering
matrix.

One of the earliest approximation methods of deter-
mining ΔS of a substitutional defect based on the pert-
urbation theory was given by Stripp and Kirkwood[6].
Another more commonly used approximation method based on
the Einstein approximation (regarding each atom in the
neighbourhood of defect to be oscillating in an average
field produced by the rest of the atoms which are held
stationary) has been given by Huntington et al.[11]. They
have obtained ΔS of a vacancy in copper by using the
Einstein approximation for calculating the contribution of
immediate neighbourhood of the vacancy to ΔS and elasticity
theory for that of the rest of the region. Nardelli and
Chiarotti[25] have calculated the entropy of a vacancy in
crystals of inert gases by using a similar approximation
method. For alkali halides, Theimer[15] and Chandra et al.[16]
have expressed ΔS in terms of the change in trace of the
dynamical matrix of the perfect crystal due to the defect
by assuming the changes in frequencies due to the defect
be small). Matthew[17] has discussed the relative reli-
ity of these approximation methods by comparing the
ts from them with the exact results for substitutional
s in linear and cubic lattices.

Recently, K. Mukherjee[26] has given a quasi-thermodynamic method of obtaining ΔS of vacancies in f.c.c. metals. This method is based on the experimental fact that the equilibrium concentration of vacancies in f.c.c. metals near the melting point lies between 10^{-4} and 10^{-3}. Subsequently, K. Mukherjee[27] has applied this method to solid argon and the results obtained are in good agreement with experimental values within the approximation of the Einstein model of solids.

We shall discuss the pseudomolecular model of finding the self-entropy of a general point defect[10] in §3.2 and §3.3, and some model calculations based on it in §3.4. §3.5 contains a discussion of the various theoretical and experimental methods of finding ΔS.

§3.2 Method Based on Pseudomolecular Frequencies

An exact method of finding the self-entropy of a general point defect based on the pseudomolecular model (discussed in Chapter II) has been given by Mahanty[10]. The expression for ΔS follows from the use of eqn. (2.19) in eqn. (3.2).

Using the notation of §2.1 in eqn. (3.2), ΔS can be written as

$$\Delta S = -\frac{k_B}{2} \ln \left[\left(\frac{\hbar}{k_B T}\right)^{2(N'-N)} \frac{|\hat{L}| \, |\hat{M}|}{|\hat{L}| \, |\hat{M}'|} \right] + (N'-N) k_B$$

$$= -\frac{k_B}{2} \ln \left[\left(\frac{\hbar}{k_B T}\right)^{2(n'-n)} \frac{|\hat{C}' - \hat{B}'^T \hat{A}^{-1} \hat{B}'| \, |\hat{m}|}{|\hat{C} - \hat{B}^T \hat{A}^{-1} \hat{B}| \, |\hat{m}'|} \right] + (N'-N) k_B$$

$$= \lim_{\omega \to 0} \left[-\frac{k_B}{2} \ln \left(\left(\frac{\hbar}{k_B T}\right)^{2(n'-n)} \frac{|\hat{C}' - \hat{B}'^T \hat{A}^{-1} \hat{B}' - \hat{m}' \omega^2| \, |\hat{m}|}{|\hat{C} - \hat{B}^T \hat{A}^{-1} \hat{B} - \hat{m} \omega^2| \, |\hat{m}'|} \right) \right] + (N'-N) k_E$$

$$= -\frac{k_B}{2} \ln \left[\left(\frac{\hbar}{k_B T}\right)^{2(n'-n)} \frac{\prod_{\sigma=1}^{n'} (\omega_\sigma'^2)}{\prod_{\mu=1}^{n} (\omega_\mu^2)} \frac{|\hat{m}|}{|\hat{m}'|} \right] + (N'-N) k_B \quad ,$$

$$(3.4)$$

here $\omega_\sigma'^2$ and ω_μ^2 are given, respectively, by the roots
f the following two equations

$$\left| \hat{C}' - \hat{B}'^T \hat{A}^{-1} \hat{B}' - \hat{m}' \omega^2 \right| = 0 \quad , \tag{3.5}$$

nd

$$\left| \hat{C} - \hat{B}^T \hat{A}^{-1} \hat{B} - \hat{m} \omega^2 \right| = \left| \lim_{\omega \to 0} \hat{G}_C^{-1}(\omega) - \hat{m} \omega^2 \right| = 0, \tag{3.6}$$

ere use has been made of eqn. (2.9) in eqn. (3.6).

Equations (3.5) and (3.6) give n' and n frequencies

ω_σ' and ω_μ, respectively) associated with region Γ_2 of
e imperfect and perfect crystals. These frequencies may
called the pseudomolecular frequencies as they have been
itten in terms of effective force constant matrices $\hat{B}'^T$
$\hat{A}^{-1} \hat{B}'$ and $\hat{B}^T \hat{A}^{-1} \hat{B}$ (of dimensions n' and n , respectively)
ich are obtainable from the effective interaction matrices
the imperfect and perfect pseudomolecules (Chapter II)
the zero frequency limit. The self-entropy of a point
fect is therefore, expressible as a function of the perturbed
unperturbed pseudomolecular frequencies in the sense

3.3   Divergence Problem in Determining G_C^{-1}

The matrix elements of $\hat{G}_C(\omega)$ occurring in eqn. (3.6) are defined by the following equation[28]

$$\hat{G}_C(\underline{\ell},\underline{\ell}';\omega) = \frac{1}{M}\sum_k \frac{\overline{V_{\underline{\ell}}(\underline{k})}V_{\underline{\ell}'}(\underline{k})}{\omega^2(\underline{k}) - \omega^2}, \qquad (3.7)$$

where $V_{\underline{\ell}}(\underline{k})$ is the ℓth component of the kth eigen vector of the dynamical matrix and $\omega^2(k)$ is the corresponding eigen-frequency. The summation in eqn. (3.7) is over all the vibrational modes of the perfect lattice. As mentioned earlier, $\hat{G}_C(\omega)$ has the point symmetry of the crystal and can, therefore, be block-diagonalised by using group-theoretical methods and then inverted. A divergence difficulty arises in this method for the limit $\omega \to 0$. From eqn. (3.7) it is obvious that the roots $\omega^2(\underline{k}) = 0$ will give divergent elements of Green functions for $\omega \to 0$. Such roots, which correspond to the translational modes of the lattice, are always present in the secular determinants of perfect and imperfect crystals. These $\omega^2(\underline{k}) = 0$ roots persist even in the contracted secular determinants of perfect and imperfect pseudomolecules.

To overcome this difficulty we construct a unitary matrix $\hat{V}$ which contains vectors corresponding to the translational modes, and other orthogonal vectors such that $\hat{V}^+ \hat{G}_C \hat{V}$ is block-diagonalised. Such a $\hat{V}$ matrix can always be constructed by taking linear combinations of the symmetry-

adapted vectors belonging to various irreducible represent-
ations (IR) of the point-symmetry group of subspace Γ_2.
It is found that with this particular choice, matrix
$\hat{V}^+ \hat{G}_C(\omega)\hat{V}$ contains a divergent block corresponding to the
translational modes. Other blocks, corresponding to the
vectors orthogonal to the translational modes, involve such
differences of the elements of $\hat{G}_C(\omega)$ that divergences in
them cancel out. The divergent terms can generally be
simplified considerably by using the sum-rules satisfied
by Green functions[29] in the zero frequency limit.

§ 3.4 Calculation of the self-entropy of a substitutional Defect and a Vacancy in Some Lattice Models

We shall give here some results of computations of the
pseudomolecular frequencies of substutional impurities and
vacancies in the square, simple cubic and b.c.c. lattices.
The interatomic interactions in the lattices are assumed to
be of the nearest-neighbour type. Relaxation of the structure
around the impurities can be included in the parameters of
the defects in the model calculations given in § 3.4a–§ 3.4c.

§ 3.4a. The Isotropic Square Lattice

(i) Substitutional impurity:

This hypothetical model is considered here to illustrate
the details of a typical calculation. For mathematical
simplicity each atom is assumed to have only one component
of displacement so that polarisation effects can be ignored.

A substitutional impurity having mass m' and force constant γ' is taken to be at the origin of subspace Γ_2 (fig (1b)), m and γ are the mass and force constant, respectively, of a normal atom (fig (1a)). Here n' = n = 5. The integral form of elements of $\hat{G}_c(\omega)$ is given by[28].

$$g(\underline{\ell}, \underline{\ell}'; \omega) \equiv g(\ell_1 - \ell_1', \ell_2 - \ell_2'; \omega)$$

$$= \frac{1}{(2\pi)^2} \int_0^{2\pi} \int_0^{2\pi} \frac{\cos((\ell_1 - \ell_1')k_1)\cos((\ell_2 - \ell_2')k_2)\,dk_1 dk_2}{2\gamma(2 - \cos k_1 - \cos k_2) - m\omega^2} \qquad (3.8)$$

In this isotropic model, $g(\underline{\ell}, \underline{\ell}'; \omega) = g(\underline{\ell}; \underline{\ell}; \omega)$. The indices needed to specify the elements of $\hat{G}_c$ are 0,1,2,3,4, where 0 refers to the impurity site and 1,2,3,4 are the nearest neighbours taken in a cyclic order, this group of atoms constituting the pseudomolecule.

The $\hat{G}_c(\omega)$ matrix is given in Appendix II. The matrix of symmetry adapted vectors $\hat{S}$ of the point symmetry group D_4 of Γ_2, and matrix $\hat{V}$ constructed out of the vectors of $\hat{S}$ as explained in §3.3 are given in Appendix III.

The Sum-rules satisfied by the Green functions are,

$$(4\gamma - m\omega^2)g(0,0;\omega) - 4\gamma g(1,0;\omega) = 1 \qquad (3.9)$$

and

$$(4\gamma - m\omega^2)g(1,0;\omega) - \gamma\Big(g(0,0;\omega) + 2g(1,1;\omega) + g(2,0;\omega)\Big) = 0$$
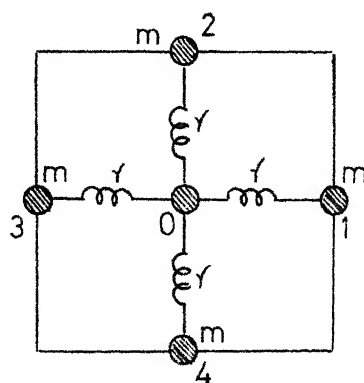
$$(3.10)$$

Isotropic square lattice
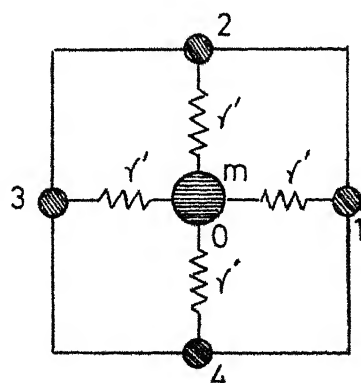

Fig. Ia   Pseudomolecule for the perfect crystal

Fig.Ib Pseudomolecule for the square lattice containing
a   substitutional impurity at the origin.

The block-diagonalised form of $\hat{G}_C(\omega)$ is

$$\hat{V}^+\hat{G}_C(\omega)\hat{V}=\begin{pmatrix} \frac{1}{20\gamma}+5g(1,0;\omega) & -\frac{1}{10\gamma} & 0 & 0 & 0 \\ -\frac{1}{10\gamma} & \frac{1}{5\gamma} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2\gamma}+(g(2,0;\omega)-g(1,0;\omega)) & 0 & 0 \\ 0 & 0 & 0 & (g(0,0;\omega)-g(2,0;\omega)) & 0 \\ 0 & 0 & 0 & 0 & (g(0,0;\omega)-g(2,0;\omega)) \end{pmatrix}$$

$$(3.11)$$

In the limit $\omega \rightarrow 0$, the divergent term occurs only in the first block which corresponds to the translational mode written in the first column of $\hat{V}$.

Inverting eqn. (3.11) and performing inverse transformation, the $\hat{G}_C^{-1}$ matrix obtained is,

$$\lim_{\omega\rightarrow 0} \hat{G}_C^{-1}(\omega)\equiv \hat{C}-\hat{B}^T\hat{A}^{-1}\hat{B}$$

$$\begin{pmatrix} 4\gamma & -\gamma & -\gamma & -\gamma & -\gamma \\ -\gamma & \frac{-\gamma(\pi^2-6+4)}{2(4-\pi)(\pi-2)} & \frac{\gamma(2-\pi)}{2(4-\pi)} & \frac{\gamma(\pi^2-2\pi-4)}{2(4-\pi)(\pi-2)} & \frac{\gamma(2-\pi)}{2(4-\pi)} \\ -\gamma & \frac{\gamma(2-\pi)}{2(4-\pi)} & \frac{-\gamma(\pi^2-6\pi+4)}{2(4-\pi)(\pi-2)} & \frac{\gamma(2-\pi)}{2(4-\pi)} & \frac{\gamma(\pi^2-6\pi-4)}{2(4-\pi)(\pi-2)} \\ -\gamma & \frac{\gamma(\pi^2-2\pi-4)}{2(4-\pi)(\pi-2)} & \frac{\gamma(2-\pi)}{2(4-\pi)} & \frac{-\gamma(\pi^2-6\pi+4)}{2(4-\pi)(\pi-2)} & \frac{\gamma(2-\pi)}{2(4-\pi)} \\ & \frac{\gamma(2-\pi)}{} & \frac{\gamma(\pi^2-2\pi-4)}{} & \frac{\gamma(2-\pi)}{} & \frac{-\gamma(\pi^2-6\pi+4)}{} \end{pmatrix}$$

where use has been made of the sum-rules given by
eqns. (3.9) and (3.10) in the limit $\omega \rightarrow 0$.

The sum of elements of each row of $\hat{G}_c^{-1}$ in eqn. (3.12) is zero
showing thereby that the pseudomolecule has a zero frequen-
cy associated with its translational mode.

The matrix $\hat{C}$ of force constants between atoms of the perfect
region is,

$$
\hat{C} = \begin{pmatrix}
4\gamma & -\gamma & -\gamma & -\gamma & -\gamma \\
-\gamma & 4\gamma & 0 & 0 & 0 \\
-\gamma & 0 & 4\gamma & 0 & 0 \\
-\gamma & 0 & 0 & 4\gamma & 0 \\
-\gamma & 0 & 0 & 0 & 4\gamma
\end{pmatrix} \tag{3.13}
$$

Matrix $\hat{B}^T \hat{A}^{-1} \hat{B}$ obtained by subtracting eqn. (3.12) from
eqn. (3.13) is,

$$
\hat{B}^T \hat{A}^{-1} \hat{B} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 4\gamma + \dfrac{\gamma(\pi^2-6\pi+4)}{2(4-\pi)(\pi-2)} & \dfrac{\gamma(\pi-2)}{2(4-\pi)} & \dfrac{-\gamma(\pi^2-2\pi-4)}{2(4-\pi)(\pi-2)} & \dfrac{\gamma(\pi-2)}{2(4-\pi)} \\
0 & \dfrac{\gamma(\pi-2)}{2(4-\;)} & 4\gamma + \dfrac{\gamma(\pi^2-6\pi+4)}{2(4-\pi)(\pi-2)} & \dfrac{\gamma(\pi-2)}{2(4-\pi)} & \dfrac{-\gamma(\pi^2-2\pi-4)}{2(4-\pi)(\pi-2)} \\
0 & -\dfrac{\gamma(\pi^2-2\pi-4)}{2(4-\pi)(\pi-2)} & \dfrac{\gamma(\pi-2)}{2(4-\pi)} & 4\gamma + \dfrac{\gamma(\pi^2-6\pi+4)}{2(4-\pi)(\pi-2)} & \dfrac{\gamma(\pi-2)}{2(4-\pi)} \\
0 & \dfrac{\gamma(\pi-2)}{2(4-\pi)} & \dfrac{-\gamma(\pi^2-2\pi-4)}{2(4-\pi)(\pi-2)} & \dfrac{\gamma(\pi-2)}{2(4-\pi)} & 4\gamma + \dfrac{\gamma(\pi^2-6\pi+4)}{2(4-\pi)(\pi-2)}
\end{pmatrix}
$$

$$\tag{3.14}$$

The matrix in eqn. (3.14) has a row and a column of zero elements corresponding to the index of interior atom O which does not interact with any of the atoms of region Γ_1. This follows from eqn. (2.13) for the elements of $\hat{B}^T \hat{A}^{-1} \hat{B}$ in the nearest neighbours interaction approximation.

The matrix $\hat{C}'$ of force constants of atoms belonging to region Γ_2 perturbed by a substitutional defect, is given as,

$$
\hat{C}' = \begin{pmatrix}
4\gamma' & -\gamma' & -\gamma' & -\gamma' & -\gamma' \\
-\gamma' & 3\gamma+\gamma' & 0 & 0 & 0 \\
-\gamma' & 0 & 3\gamma+\gamma' & 0 & 0 \\
-\gamma' & 0 & 0 & 3\gamma+\gamma' & 0 \\
-\gamma' & 0 & 0 & 0 & 3\gamma+\gamma'
\end{pmatrix} \quad (3.15)
$$

In this case matrix $\hat{B}^{T'} \hat{A}^{-1} \hat{B}'$ is exactly identical with the matrix $\hat{B}^T \hat{A}^{-1} \hat{B}$ given by eqn. (3.14).

The perturbed pseudomolecular frequencies obtained by substituting eqns. (3.14) and (3.15) in eqn. (3.5) are,

$$
\omega_0' = 0; \quad \omega_1'^2 = \frac{4m+m'}{mm'}\gamma';
$$

$$
\omega_2'^2 = \frac{\gamma'}{m} + \frac{2\gamma(\pi-2)}{m(4-\pi)}
$$

(3.16)

and

$$
\omega_3'^2 = \omega_4'^2 = \frac{\gamma'}{m} + \frac{2\gamma}{m(\pi-2)}
$$

The unperturbed pseudomolecular frequencies can be obtained by solving eqn. (3.6) or by taking the limit $\gamma' \rightarrow \gamma$ and $m' \rightarrow m$ in eqn. (3.16). These, therefore, are given by,

$$\omega_o^2 = 0; \quad \omega_1^2 = \frac{5\gamma}{m}; \quad \omega_2^2 = \frac{\gamma\pi}{m(4-\pi)}$$

and

$$\omega_3^2 = \omega_4^2 = \frac{\gamma\pi}{m(\pi-2)} \tag{3.17}$$

Substituting eqns. (3.17) and (3.16) (dropping out $\omega_o'^2 = \omega_o^2 = 0$) in eqn. (3.4) the self entropy can be written down in terms of parameters γ', γ, m' and m of the lattice.

(ii)   Vacancy in the Square Lattice

In the scalar model considered here a vacancy decreeses the number of degrees of freedom associated with $\lceil_2$ by one (i.e., $n - n' = 1$). Matrices $\hat{C}'$ and $\hat{B}'^T \hat{A}^{-1} \hat{B}'$ are therefore (4x4) matrices. If the vacant site is taken to be at the origin of region $\lceil_2'$, matrix $\hat{B}'^T \hat{A}^{-1} \hat{B}'$ can be obtained from $\hat{B}^T \hat{A}^{-1} \hat{B}$ (i.e., eqn. 3.14) by deleting the first row and first column of zero elements (§2.2).

Matrix $\hat{C}'$ is given as,

$$\hat{C}' = 3\gamma \hat{I}, \tag{3.18}$$

where

$$\hat{I} = (4\text{x}4) \text{ unit matrix.}$$

The pseudomolecular frequencies in this case can be shown to be[10],

$$\omega_1^2 = 0; \quad \omega_2^2 = \frac{2\gamma}{m}\left(\frac{\pi-2}{4-\pi}\right)$$

$$\omega_3^2 = \omega_4^2 = \frac{2\gamma}{m(\pi-2)} \tag{3.19}$$

3.4b   The Isotropic Simple Cubic Lattice

(i)   Perfect Lattice:

Consider a simple cubic lattice consisting of atoms of mass m each and nearest neighbour force constants Υ . The atoms are located at the sites $\underline{a}_\ell$ given by

$$\underline{a}_\ell = \ell_1 a\hat{i} + \ell_2 a\hat{j} + \ell_3 a\hat{k},\qquad (3.20)$$

where

$$\underline{\ell} = (\ell_1, \ell_2, \ell_3) \text{ and a is the lattice constant.}$$

An atom at the origin $(0,0,0)$ and its six nearest neighbours at lattice sites $(1,0,0)$; $(0,1,0)$; $(0,0,1)$; $(\bar{1},0,0)$; $(0,\bar{1},0)$; and $(0,0,\bar{1})$, as shown in Fig. (2), shall be taken as the atoms constituting a pseudomolecule. The elements of Green function matrix $\hat{G}_c(\omega)$ are given by the following integrals[28],

$$g(\underline{\ell},\underline{\ell}';\omega) = \frac{1}{(2\pi)^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \frac{d^3k\; e^{i\underline{k}\cdot(\underline{\ell}-\underline{\ell}')}}{2\Upsilon(3-\cos k_1-\cos k_2-\cos k_3)-m\omega^2}$$

$$(3.21)$$

Using group-theoretical methods, the subspace Γ_2 can be reduced into the following IRs of O_h group

$$\Gamma_2 = 2A_{1g}+F_{1u}+E_g \qquad (3.22)$$

$\hat{V}$ and $\hat{C}$ matrices are given in Appendix IV. Appendix IV also contains $\hat{V}^+\hat{G}_c\hat{V}$ and the matrix $\hat{B}^T \hat{A}^{-1}\hat{B}$ obtained from them. Using these in eqn. (3.6), the unperturbed pseudo-molecular frequencies obtained are,
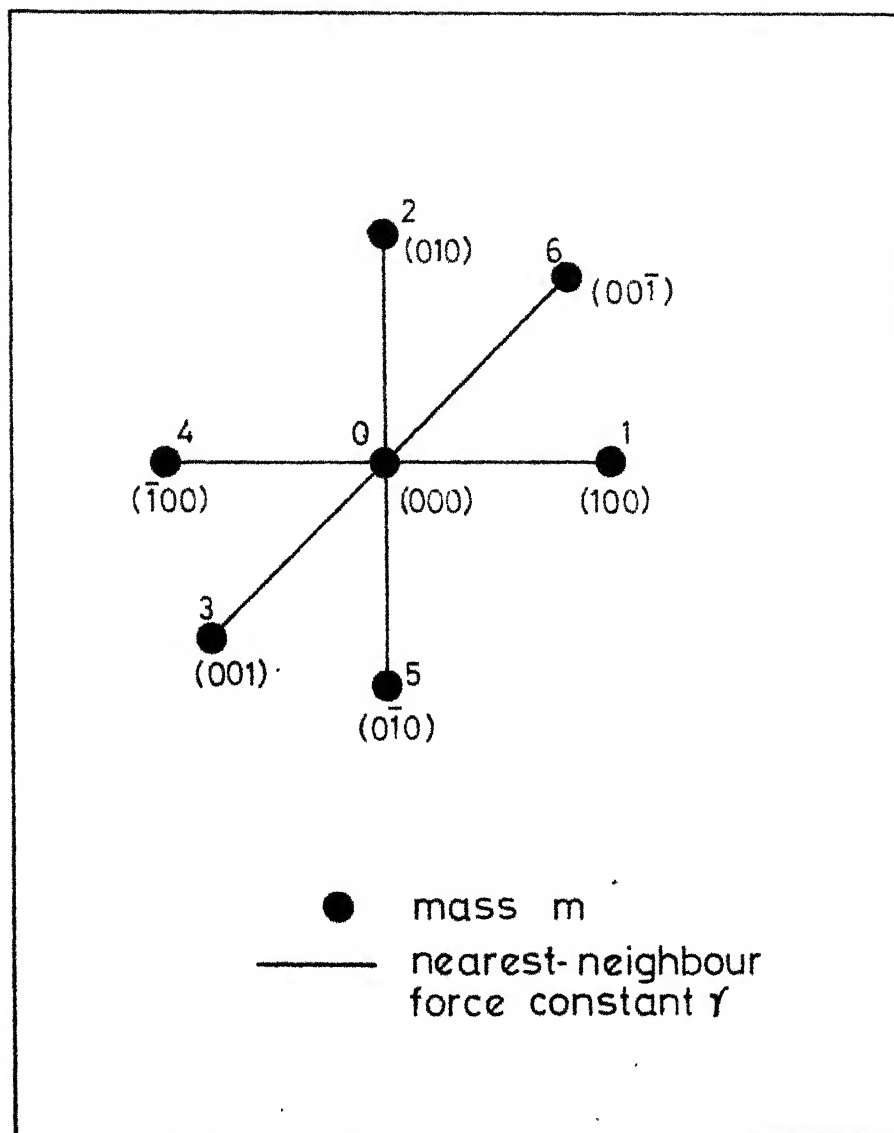
Fig. 2 Pseudomolecule for the perfect isotropic simple cubic lattice (§ 3·4b).

$$\omega_1^2 = 0; \quad \omega_2^2 = \frac{7\delta}{m} \qquad : \qquad A_{1g} - IR , \qquad (3.23)$$

$$\omega_3^2 = \omega_4^2 = \omega_5^2 = \frac{1}{m\left[g(0,0;0)-g(2,0,0)\right]} = 4.762\,\frac{\gamma}{m}: F_{1u}-IR,$$

$$(3.24)$$

$$\omega_6^2 = \omega_7^2 = \frac{1}{m\left[g(0,0,0)+g(2,0,0)-g(1,1,0)\right]} = 5.417\,\frac{\gamma}{m}: E_g-IR,$$

$$(3.25)$$

where the numerical values of Green functions computed by Fourier-series method[30] have been used.

ii) <u>Substitutional Defect at the Origin:</u>

For a substitutional defect of mass m' and force constant γ' placed at the origin of subspace Γ_2, $\hat{C}'$ has the following form

$$\hat{C}' = \begin{pmatrix} 7\gamma' & -\gamma' & -\gamma' & -\gamma' & -\gamma' & -\gamma' & -\gamma' \\ -\gamma' & 6\gamma+\gamma' & 0 & 0 & 0 & 0 & 0 \\ -\gamma' & 0 & 6\gamma+\gamma' & 0 & 0 & 0 & 0 \\ -\gamma' & 0 & 0 & 6\gamma+\gamma' & 0 & 0 & 0 \\ -\gamma' & 0 & 0 & 0 & 6\gamma+\gamma' & 0 & 0 \\ -\gamma' & 0 & 0 & 0 & 0 & 6\gamma+\gamma' & 0 \\ -\gamma' & 0 & 0 & 0 & 0 & 0 & 6\gamma+\gamma' \end{pmatrix}$$

$$(3.26)$$

The matrix $\hat{B}'^T \hat{A}^{-1} \hat{B}'$ is identical with matrix $\hat{B}^T \hat{A}^{-1} \hat{B}$ given in Appendix IV.

The perturbed pseudomolecular frequencies are,

$$\omega_1'^2 = 0, \qquad \omega_2'^2 = \frac{6m+m'}{mm'}\gamma' \quad : \quad A_{1g}-IR \ ,$$

$$\omega_3'^2 = \omega_4'^2 = \frac{1}{m}\left[\frac{1}{g(0,0,0)-g(2,0,0)} + \gamma'-\overline{\gamma}\right]$$

$$= \frac{\gamma'+3.762\gamma}{m} \quad : \quad F_{1u}-IR,$$

$$\omega_6'^2 = \omega_7'^2 = \frac{1}{m}\left[\frac{1}{g(0,0,0)+g(2,0,0)-2g(1,1,0)} + \gamma'-\overline{\gamma}\right]$$

$$= \frac{\gamma'+4.417\gamma}{m} \quad : \quad E_g-IR \quad .$$

$$(3.27)$$

(iii) Vacancy at the Origin:

For a vacancy at the origin $(0,0,0)$, matrix $\hat{C}'$ can be written as

$$\hat{C}' = 5\gamma\hat{I}, \qquad (3.28)$$

where $\hat{I}$ is a (6x6) unit matrix.

$\hat{B}'^T \hat{A}^{-1} \hat{B}'$ is a (6x6) matrix and is obtained from $\hat{B}^T \hat{A}^{-1} \hat{B}$ (Appendix IV) by deletion of the first row and first column.

The eigen-frequencies obtained are,

$$\omega_1''^2 = 0 \qquad : A_{1g}-IR \ ,$$

$$\omega_2''^2 = \omega_3''^2 = \omega_4''^2 = \frac{1}{m}\left[\frac{1}{g(0,0,0)-g(2,0,0)} -\gamma\right]$$

$$= 3.762\,\frac{\gamma}{m} \qquad : F_{1u}-IR,$$

$$\omega_5''^2 = \omega_6''^2 = \frac{1}{m}\left[\frac{1}{g(0,0,0)+g(2,0,0)-2g(1,1,0)} -\gamma\right] \quad (3.29)$$

$$= 4.417\,\frac{\gamma}{m} \qquad : E_g-IR$$

It may be mentioned here that each set of frequencies given by eqns. (3.26)-(3.28) occurs three-times as the X, Y and Z components of atomic displacements are decoupled in the scalar model considered here.

3.4c   The B.C.C. Lattice

The model chosen here is the one that has been used earlier in connection with the phonon scattering[31]. The nearest neighbour central and non-central force constants are γ_1 and γ_2. The equations of motion are written in terms of the constants β_1 and β_2 which are defined as,

$$\beta_1 = \frac{\gamma_1 + \gamma_2}{3} \; ; \quad \beta_2 = \frac{\gamma_1 - \gamma_2}{3} \qquad (3.30)$$

$\hat{V}$ matrix used here is given in Appendix V.   It contains three transitional vectors corresponding to translations in X, Y and Z directions.

The calculations have been done for a substitutional impurity.   In the limit $\beta_2 \to 0$, the results have also been obtained for a vacancy.   In this limit the three components of the displacement of each atom get decoupled in a manner analogous to the previous example of the simple cubic lattice.

The unperturbed pseudomolecular frequencies are given by the roots of the following equation,

$$\left\{(-m\omega^2)x\left(m^2\omega^4-m\omega^2(\frac{X+U}{XU-Y2})+\frac{1}{XU-Y2}\right)\right\}_{3F_{1u}}^3 X\left(\frac{1}{E}-m\omega^2\right)_{A_{1g}}$$

$$X\left(\frac{1}{F}-m\omega^2\right)_{E_g}^2 X\left\{m^2\omega^4-m\omega^2(\frac{K+M}{KM-2L2})+\frac{1}{KM-2L2}\right\}_{2F_{2g}}^3 X\left(\frac{1}{N}-m\omega^2\right)_{A_{2u}}$$

$$X\left(\frac{1}{P}-m\omega^2\right)_{F_{2u}}^3 X\left(\frac{1}{R}-m\omega^2\right)_{F_{1g}}^3 X\left(\frac{1}{S}-m\omega^2\right)_{E_u}^2 = 0 \qquad (3.31)$$

and the perturbed pseudomolecular frequencies are given
by the roots of the following equation:

$$\left|\Delta(\omega)\right|_{3F_{1u}}^3 X\left(\frac{1}{E}+\Delta\beta_1-2\Delta\beta_2-m\omega^2\right)_{A_{1g}} X\left(\frac{1}{F}+\Delta\beta_1+\Delta\beta_2-m\omega^2\right)_{E_g}$$

$$X\left\{m^2\omega^4-m\omega^2(\frac{K+M}{KM-2L2}+2\Delta\beta_1-\Delta\beta_2)+\frac{1+(\Delta\beta_1-\Delta\beta_2)K+\Delta\beta_1M-4\Delta\beta_2L}{KM-2L^2}\right.$$

$$\left.+(\Delta\beta_1-\Delta\beta_2)\Delta\beta_1-2\Delta\beta_2^2\right\}_{2F_{2g}}^3 X\left(\frac{1}{N}+\Delta\beta_1-2\Delta\beta_2-m\omega^2\right)_{A_{1u}}$$

$$X\left(\frac{1}{P}+\Delta\beta_1+\Delta\beta_2-m\omega^2\right)_{F_{2u}}^3 X\left(\frac{1}{R}+\Delta\beta_1+\Delta\beta_2-m\omega^2\right)_{F_{1g}}^3$$

$$X\left(\frac{1}{S}+\Delta\beta_1+\Delta\beta_2-m\omega^2\right)_{E_u}^2 = 0 \qquad (3.32)$$

where

$$\Delta(\omega)\Big|_{3F_{1u}} = \begin{vmatrix} -(m+\frac{\Delta m}{9})\omega^2 & \frac{\sqrt{8}}{9}\Delta m\omega^2 & 0 \\ \frac{\sqrt{8}}{9}\Delta m\omega^2 & \frac{X}{UX-Y2}+9\Delta\beta_1-(m+\frac{8\Delta m}{9})\omega^2 & \frac{-Y}{UX-Y2}-3\sqrt{2}\Delta\beta_2 \\ 0 & \frac{Y}{UX-Y2}-3\sqrt{2}\Delta\beta_2 & \frac{U}{UX-Y2}-\Delta\beta_2+\Delta\beta_1 \\ & & -m\omega^2 \end{vmatrix}$$

$$(3.33)$$

with $\Delta m = m'-m$; $\Delta\beta_1 = \beta_1' - \beta_1$; $\Delta\beta_2 = \beta_2' - \beta_2$ and in the notation of Green functions used earlier[31],

$$E = (g_{Do}-g_{D4}) + (g_{D32}-g_{D21}) + 2(g_{D22}-g_{D31}) + 2(g_{N4}+g_{N3}) \; ;$$

$$F = (g_{Do}-g_{D4}) + (g_{D32}-g_{D21}) + (g_{D22}-g_{D31}) - g_{N3}-g_{N4} \quad ;$$

$$K = (g_{Do}-g_{D4}) + (g_{D21}-g_{D32}) + (g_{N3}+g_{N4}) ;$$

$$L = (g_{N4}-g_{N3}) ;$$

$$M = (g_{Do}-g_{D4}) + (g_{D32}-g_{D21}) + 2(g_{D22}-g_{D31}) ;$$

$$N = (g_{Do}-g_{D22}) + (g_{D4}-g_{D22}) + (g_{D21}-g_{D31}) + (g_{D32}-g_{D31}) + 2(g_{N3}-g_{N4}) ,$$

$$P = (g_{Do}-g_{D21}) + (g_{D4}-g_{D32}) - g_{N4}-g_{N3} \quad ;$$

$$R = (g_{Do}-g_{D4}) + (g_{D21}-g_{D32}) - g_{N4}-g_{N3} ;$$

$$S = (g_{Do}-g_{D22}) + (g_{D21}-g_{D22}) + (g_{D4}-g_{D31}) + (g_{D_{32}}-g_{D31}) + (g_{N4}-g_{N3}) ;$$

$$U = \frac{1}{9}\left\{ 9(g_{Do}-g_{D1}) + (g_{D4}-g_{D_1}) + (g_{D21}-g_{D1}) + 2(g_{D22}-g_{D1}) + 2(g_{D31}-g_{D1}) \right.$$
$$\left. + (g_{D32}-g_{D1})\right\} ;$$

$$X = (g_{Do}-g_{D21}) + (g_{D4}-g_{D32}) - (g_{N4}-g_{N3}) ;$$

$$Y = \frac{\sqrt{2}}{3}\left(8g_{N1}-g_{N4}-g_{N3} \right). \tag{3.34}$$

In the limit $\beta_2 \longrightarrow 0$ and $\beta_1 = \gamma$, $\beta_1' = \gamma'$, all the non-diagonal Green functions g_{N1}, g_{N3} and g_{N4} become zero and $g_{D21} = g_{D22}$; $g_{D31} = g_{D32}$[31]. The Green functions satisfy the following sum-rules,

$$8g_{Do} - 8g_{D1} = 1/\tau$$

$$8g_{D1} - (g_{Do} + g_{D4} + 3g_{D21} + 3g_{D31}) = 0 \quad (3.35)$$

Using eqns. (3.35) in eqn. (3.32) the secular equation for the perturbed pseudomolecule becomes,

$$(-\omega^2)^3 \times \left\{ (m + \tfrac{\Delta m}{9}) \left[9\gamma' - (m + \tfrac{8}{9}\Delta m)\omega^2 \right] + \tfrac{8}{81}(\Delta m)^2 \omega^2 \right\}^3$$

$$\times \left\{ \tfrac{1}{X} + \gamma' - \gamma - m\omega^2 \right\}^9 \times \left\{ \tfrac{1}{E} + \gamma' - \gamma - m\omega^2 \right\}^9 \times \left\{ \tfrac{1}{M} + \gamma' - \gamma - m\omega^2 \right\}^3 = 0$$

$$(3.36)$$

The secular equation for a vacancy in this model is given by

$$\left\{ -m\omega^2 \right\}^3 \left(\tfrac{1}{X} - \gamma - m\omega^2 \right)^9 \left(\tfrac{1}{E} - \gamma - m\omega^2 \right)^9$$

$$\times \left(\tfrac{1}{M} - \gamma - m\omega^2 \right)^3 = 0$$

$$(3.37)$$

§3.5 Discussion

Experimental values of $\triangle S$ are generally derived from the data on equilibrium concentration of defects as a function of temperature. The equilibrium concentration of defects of a given type, C, at a temperature T is given by

$$C = \exp\left(\frac{\triangle S}{k_B T}\right)\exp\left(-\frac{\triangle E}{k_B T}\right) , \qquad (3.38)$$

where $\triangle E$ is the energy required for formation of a defect and $\triangle S$ is the change in entropy (exclusive of configurational entropy) due to the defect.

It has been observed experimentally that the specific heat of crystals near the melting points shows an anomalous increase from its expected linear behaviour due to the first-order anharmonic terms[32]. The anomaly in specific heat is attributed to the formation energies of vacancies. Kraftmakher et al.[33] have reported a substantial amount of data on the concentration of vacancies in various substances (e.g. tungsten, molybdenum, Copper etc.) by measuring specific heat by modulation method (amplitude of temperature oscillations produced in the sample due to a current with constant and alternating components is related to the specific heat). Chekhovska and Zhukova[34] have used the method of mixtures for concentration of vacancies in niobium. Calorimetric method has been used by Leibowitz et al.[35] for measurement of enthalpy of tungsten at

temperatures from 2800°K to 3600°K. Due to the volume of formation of vacancies, thermal expansion of solids also shows an anomalous increase at high temperatures. Kraftmakher[36] has obtained a concentration of 0.8% of vacancies in platinum (near the melting point) from the anomaly in thermal expansion. A discussion of such measurements has been given by Matthew[37]. The variations in ΔS of a vacancy, obtained from experiments on different substances, are rather large and it is inferred that some premelting phenomena and higher order anharmonic effects also contribute to the anomalies. Matthew has pointed out that these experiments might explain some premelting phenomena mainly as it is difficult to separate the effect of vacancy formation from other effects.

A large number of accurate estimates of ΔS of a vacancy based on the lattice parameter and bulk density measurements have been reported. The difference between bulk density, ρ, and the density deduced from the lattice parameter, ρ_x, is assumed to be due to vacancies such that

$$\frac{n}{N} = (\rho_x - \rho)/\rho_x = 3\left(\frac{\Delta L}{L} - \frac{\Delta a}{a}\right) \quad , \quad (3.39)$$

where n is the number of vacancies in a crystal containing N lattice sites. Δa and ΔL are the changes in average interatomic spacing a (obtained by X-ray method) and length L of the specimen, respectively. Recent papers by Smith and Chapman[38] and Simmon et al.[39] have listed a number of experiments exploiting this method. Coufal et al.[40]

have measured $\triangle L$ of solid Krypton interferrometerically
(accuracy more than 1%) for temperatures from 4 to 115°K.
Interferrometric measurements have also been used for
determining the equilibrium vacancy concentration in KCl
by von Guerard et al.[41].

For phenomena like diffusion, ionic conductivity etc.
which depend on motion of defects, an equation similar to
eqn. (3.38) holds for rate change. Measurements of ionic
conductivity σ as a function of temperature gives inform-
ation on $\triangle S$ for a number of defects (log σ T vs. 1/T
consists of straight lines in the high and low temperature
regions due to different charge carriers). Experimental
values are derived by least square computer fitting of the
data on σ. Allnatt and Pantelis[42] have given a tentative
explanation of the high temperature ($> 750°$ C) anomaly in σ
of NaCl in terms of cationic Frenkel disorder. Bauer and
Whitmore[43] have observed certain non-random deviations
between the experimental results and theoretical results
(based on presence of interacting cation and anion vacancies)
on the ionic conductivity of NaF doped with CaF_2 which may
be due to the presence of some other defects (e.g. trivacancies,
interstitials etc.). Barr and Lidiard[44] have reviewed the
properties of defects in ionic lattices.

Peterson[45] has discussed diffusion in metals in detail
in a recent review article. Mention may also be made of a

recent experiment on self-diffusion in selenium by Bratter and Gobrech[46] which shows that the equibrium vacancy concentration in semiconductors is several orders of magnitude smaller than that in metals.

W. de Sorbo[47] has given data on the energy evolved on annealing quenched in impurities in Au. Concentration of vacancies can be obtained by combining it with data on the change in resistivity due to formation of vacancies. Recently, Polakova et al.[48] have reported concentration of vacancies in nickel from quenching experiments.

Among the theoretical results, the exact numerical value of ΔS of a substitutional isotope defect obtained by Nardelli and Tettamanzi[13] is based on the distribution function of square frequencies computed numerically by Overton and Dent. They have shown that the Einstein approximation and perturbation method give results consistent with their calculations only for very light isotopes and overestimate ΔS otherwise. Nardelli and Terzi[14] find that the entropy of a vacancy at constant volume exceeds by nearly 10 percent the value obtained from the Einstein model. This shows, as pointed out by Nardelli and Terzi, that Huntington et al.[11] have underestimated the contribution, to ΔS, of perturbation due to the loss of coupling around the vacancy. Matthew[17] has shown that the Einstein approximation gives exact results for isotope defects in cubic lattices, and, in situations in which the force constants are changed, it always lies between the exact result and the trace approximation.

The pseudomolecular method for determination of ΔS can be used for a general type of defect (i.e., N' may not be equal to N) by a proper choice of the pseudo-molecule. In the present model calculations of ΔS, the changes in force-constants due to relaxation of the medium around the defect can be included in the parameters occur-ring in the effective force constant matrix, $\hat{C}'-\hat{B}'^T\hat{A}^{-1}\hat{B}'$, used for determining the pseudomolecular frequencies.

CHAPTER IV

DETAILED DYNAMICS OF A POINT DEFECT

§ 4.1   Time-Dependent Dynamics

In this section we shall briefly review the use of
partitioning technique for studying the time-dependence of
atomic displacements in the defect region with certain
initial conditions on the lattice.

The equations of motion of a perfect lattice having
N degrees of freedom is (eqn. (2.1)),

$$\hat{M} \frac{d^2}{dt^2} \underline{X}(t) = \hat{L} \underline{X}(t) \tag{4.1}$$

From the theory of Fourier transforms it is known
that if a function f and its derivatives Df, D^2f, ...,
$D^{K-1}f$ have jumps ϵ_o, ϵ_o', ..., ϵ_o^{K-1} at t = 0 only, the
Fourier-transform of the Kth derivative of f, $\Phi\left[D^K f\right]$, is
given by[49],

$$\Phi(D^K f) = (i\omega)^K \Phi(f) - \left[(i\omega)^{K-1}\epsilon_o + (i\omega)^{K-2}\epsilon_o' + \ldots + \epsilon_o^{K-1}\right] \tag{4.2}$$

Taking the Fourier-transform of eqn. (4.1) and using
eqn. (4.2) we get

$$-\omega^2 \underline{U}(\omega) - \left[i\omega\underline{X}(0) + \dot{\underline{X}}(0)\right] = \hat{L}\, \underline{U}(\omega) \tag{4.3}$$

where $\underline{X}(0)$ and $\dot{\underline{X}}(0)$ represent the initial displacement
and velocity vectors, respectively. $\underline{U}(\omega)$, the Fourier-
transform of $\underline{X}(t)$, is defined as,

$$\underline{U}(\omega) = \int_{-\infty}^{+\infty} \underline{X}(t) \; e^{i\omega t} \; dt \tag{4.4}$$

It is presumed that $\underline{X}$ and all its time-derivatives vanish for $t < o$.

We partition the matrices of eqn. (4.3) as follows,

$$\hat{M} = \begin{pmatrix} \hat{M}_A & 0 \\ 0 & \hat{m} \end{pmatrix} \quad ; \quad \underline{U}(\omega) = \begin{pmatrix} \underline{U}_1(\omega) \\ \underline{U}_2(\omega) \end{pmatrix}$$

$$\tag{4.5}$$

$$(\hat{L}-\hat{M}\omega^2) = \begin{pmatrix} \hat{A}-\hat{M}_A\omega^2 & \hat{B} \\ \hat{B}^T & \hat{C}-\hat{m}\omega^2 \end{pmatrix} \quad ; \quad (\hat{L}-\hat{M}\omega^2)^{-1} = \begin{pmatrix} \hat{G}_A(\omega) & \hat{G}_B(\omega) \\ \hat{G}_B^T(\omega) & \hat{G}_C(\omega) \end{pmatrix}$$

The diagonal submatrices in eqns. (4.5) refer to regions Γ_1 and Γ_2, respectively, of the crystal. The region Γ_2 will be subsequently affected by the point defect. The matrices corresponding to those defined in eqns. (4.5) for the imperfect crystal shall be primed except the sub-matrices $(\hat{A}-\hat{M}_A\omega^2)$ and $(\hat{M}_A)$ which remain unperturbed by the defect.

Using eqns. (4.5) in eqn. (4.3) we get the following sets of equations,

$$(\hat{A}-\hat{M}_A\omega^2)\underline{U}_1(\omega) + \hat{B}\underline{U}_2(\omega) = i\omega\hat{M}_A\underline{X}_1(0) + \hat{M}_A\underline{\dot{X}}_1(0) \tag{4.6}$$

$$\hat{B}^T\underline{U}_1(\omega) + (\hat{C}-\hat{m}\omega^2)\underline{U}_2(\omega) = i\omega\hat{m}\underline{X}_2(0) + \hat{m}\underline{\dot{X}}_2(0) \tag{4.7}$$

The required equation for $\underline{X}_2(t)$ can be obtained by eliminating $\underline{U}_1(\omega)$ from eqns. (4.6) and (4.7) and taking the inverse Fourier-transform of $\underline{U}_2(\omega)$ so obtained. The equation for $\underline{U}_2(\omega)$ is,

$$(\hat{C}-\hat{m}\omega^2-\hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B})\underline{U}_2(\omega) = i\omega\hat{m}\underline{X}_2(0)+\hat{m}\underline{\dot{X}}_2(0)$$

$$-(\hat{A}-\hat{M}_A\omega^2)^{-1}\left\{ i\omega\hat{M}_A\underline{X}_1(0) \right.$$

$$\left. + \hat{M}_A\underline{\dot{X}}_1(0) \right\} \qquad (4.8)$$

We choose the initial conditions such that only the pseudomolecular atoms have non-zero initial displacements and all the atoms have zero initial velocity i.e.,

$$\underline{X}_1(0) = \underline{\dot{X}}_1(0) = \underline{\dot{X}}_2(0) = 0$$

and

$$\underline{X}_2(0) \neq 0 \qquad (4.9)$$

This particular set of initial conditions is chosen as it simplifies the mathematics considerably and is applicable in many physical situations.

Substituting eqns. (4.9) in eqn. (4.8) we get,

$$\left[(\hat{C}-\hat{m}\omega^2)-\hat{B}^T(\hat{A}-\hat{M}_A\omega^2)^{-1}\hat{B}\right] \underline{U}_2(\omega) = i\hat{m}\omega\underline{X}_2(0) \qquad (4.10)$$

Using eqn. (2.9) in eqn. (4.10) we get the following equation for $\underline{U}_2(\omega)$

$$\underline{U}_2(\omega) = i\omega\,\hat{G}_c(\omega)\hat{m}\,\underline{X}_2(0) \qquad (4.11)$$

In the presence of a point defect, equation for the Fourier transform of the displacement vector of the pseudo-molecular atoms, $\underline{U}_2'(\omega)$, can be written in analogy with equation (4.10) as

$$\left[\hat{C}' - \hat{m}' \omega^2 - \hat{B}'^T (\hat{A} - \hat{M}_A \omega^2)^{-1} \hat{B}' \right] \underline{U}'_2(\omega) = i m' \omega \underline{X}'_2(0) \tag{4.12}$$

Using eqns. (2.9) and (2.15) in eqn. (4.12) we get

$$\underline{U}'_2(\omega) = i\omega \left[\hat{C}' - \hat{m}' \omega^2 + \left[\hat{G}_c^{-1}(\omega) - \hat{C} + \hat{m}\omega^2 \right]_{c,a} \right]^{-1} \hat{m}' \underline{X}'_2(0) \tag{4.13}$$

4.2 Spectral Density Function of a Normal Mode

A transformation to the normal mode co-ordinates can be performed by applying a unitary matrix $\hat{S}$, constructed out of the symmetry adapted vectors of the point symmetry group of the crystal, to the displacement vector $\underline{X}_2(t)$. It simplifies the calculations considerably as the various matrices occurring in eqns. (4.12) and (4.13) can be block-diagonalised by this transformation.

Taking the Fourier-transform of eqn. (4.13) we get

$$\underline{X}'_2(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} i\omega \left[(\hat{C}' - \hat{m}' \omega^2) + (\hat{G}_c^{-1}(\omega) - \hat{C} + \hat{m}\omega^2)_{c,a} \right]^{-1} \hat{m}' \underline{X}'_2(0) e^{i\omega t} d\omega \tag{4.14}$$

Transformation to the normal co-ordinates can be written as

$$\underline{Y}'_2(t) = \hat{S}^+ \underline{X}'_2(t) \tag{4.15}$$

Substituting eqn. (4.14) in eqn. (4.15), the time-dependence of normal modes of the atoms constituting the imperfect pseudomolecule, $\underline{Y}'_2(t)$, can be written in matrix notation as

$$\underline{Y}'_2(t) = \int_{-\infty}^{+\infty} \hat{J}(\omega) \underline{Y}'_2(0) e^{i\omega t} d\omega \tag{4.16}$$

where

$$\hat{J}(\omega) = \frac{i\omega}{2\pi} \left[\hat{S} + \left\{ (\hat{C}' - \hat{m}'\omega^2) + (\hat{G}_c^{-1}(\omega) - \hat{C} + \hat{m}\omega^2)_{c,a} \right\} \hat{S} \right]^{-1} \hat{S} + \hat{m}'\hat{S}$$

(4.17)

and

$$\underline{Y}_2'(0) = S^+ \underline{X}_2'(0)$$

(4.18)

From eqn. (4.16) the time-dependence of a particular normal co-ordinate $y_\nu'(t)$ is expressible as,

$$y_\nu'(t) = \int_{-\infty}^{+\infty} J_\nu(\omega) e^{i\omega t} d\omega ,$$

(4.19)

where

$$J_\nu(\omega) = \sum_\mu (\hat{J}(\omega))_{\nu\mu} (\underline{Y}_2'(0))_\mu$$

(4.20)

We use the following theorem to find the time-asymptotic form of $y_\nu'(t)$. It states that if a function $f(x)$ satisfies the following conditions,

(1) It has a finite number of singularities at $X = X_1$, X_2, X_3, ----X_M ;

(2) $f(X) - F_m(X)$ has absolutely integrable N^{th} derivative in the interval including X_m (for all m from 1 to M), where $F_M(X)$ is a linear combination of functions having the nature of singularity at $X = X_{m'}$;

(3) $f^N(X)$, the Nth derivative of $f(X)$, is well behaved at infinity,

the Fourier-transform of $f(x)$ viz. $g(y)$ satisfies the following equation[50]

$$g(Y) = \sum_{m=1}^{M} G_m(Y) + O(|Y|^{-N}) \qquad \text{as} \qquad |Y| \longrightarrow \infty , \qquad (4.21)$$

where $G_m(Y)$ is the Fourier-transform of $F_m(X)$. $G_m(Y)$ for some of the functions $F_m(X)$, corresponding to some general types of singularities, have been tabulated[50]

Using this result Montroll and Mazur[51] and Baroody[52] have obtained the asymptotic forms of momentum autocorrelation functions which are written in terms of the frequency distribution function. Montroll and Mazur have given results for the two-dimensional and three-dimensional lattices by finding the contributions from van Hove singularities of the frequency distribution functions.

The exact evaluation of integrals in eqn. (4.19) is quite difficult because of the complicated nature of $J_\nu(\omega)$ in most of the cases. $J_\nu(\omega)$ may be called the spectral density function of νth normal mode of vibration. We can study the asymptotic time-behaviour of $y'_\nu(t)$ by applying the above-mentioned theorem. From eqns. (4.19) and (4.21) it is clear that the isolated singularities and critical points of $J_\nu(\omega)$ will give non-zero contributions to $y'_\nu(t)$ for $t \longrightarrow \infty$. Qualitatively, therefore, the well-behaved part of the spectral density function $J_\nu(\omega)$ gives relaxing modes of vibrations and, the singularities and critical points correspond to persistent vibrations. The time-dependence of a normal vibrational mode of the pseudo-molecule is thus expressible as a superposition of the

relaxing and persistent vibrations. The persistent modes having frequencies within the continuum shall represent resonance modes. An estimate of the width of any such mode, if present, can be obtained by substituting some values of the defect parameters and Green functions in the equation which determines frequency of the resonant mode. The singularities of $J_\nu(\omega)$ outside the continuum give rise to localized vibrational modes.

A sum-rule relating the trace of spectral density matrix $\hat{J}(\omega)$ of the perfect pseudomolecule with the frequency distribution function can be derived as follows: From eqn. (4.18) $\hat{J}(\omega)$ for the perfect pseudomolecule can be written as

$$\hat{J}(\omega) = \frac{i\omega}{2\pi} \hat{S}^{+} \hat{G}_{c}(\omega)\hat{S}\, m$$

$$\text{Trace } \hat{J}(\omega) = \frac{im\omega}{2\pi} \text{Trace } \hat{G}_{c}(\omega)$$

$$= \frac{im\omega}{2\pi} n\, g(000;\omega), \qquad (4.22)$$

where the Green function $g(000;\omega)$ is defined by

$$g(000;\omega) = \frac{1}{mN} \sum_{\underline{k},j} \frac{1}{\omega_j^2(k) - \omega^2 - i\epsilon} \quad (\epsilon \rightarrow 0)$$

$$(4.23)$$

and n is the number of degrees of freedom associated with subspace Γ_2' of the perfect crystal.

From equations (4.22) and (4.23) we have

Real part $\left[\text{Trace } \hat{\jmath}(\omega)\right] = \dfrac{\omega\, n}{2\pi N}\displaystyle\sum_{\underline{k},j} \delta\,(\omega^2 - \omega_j^2(k))$

$$= \dfrac{\omega\, n}{2\pi N}\,\rho(\omega^2), \qquad (4.24)$$

where $\rho(\omega^2)$ is the distribution function of squared-frequencies.

4.3 Isotope Defect in the Linear Chain

The time-dependence of displacement of an isotope defect of mass m' from its equilibrium position, in a linear chain of atoms of mass m /and nearest neighbour force constant γ, is given by using eqn. (4.14) as,

$$X(t) = \dfrac{i m' X(0)}{2\pi}\int_{-\infty}^{+\infty}\dfrac{e^{i\omega t}\, g(0;\omega)\, d\omega}{1-(m'-m)\omega^2 g(0;\omega)}, \qquad (4.25)$$

where X(0) is initial displacement of the impurity from its equilibrium position.

From eqn. (4.25)

$$X(t) = -\dfrac{m' X(0)}{\pi}\int_0^{\infty}\dfrac{\omega \sin(\omega t)\, g(0;\omega)\, d\omega}{1-(m'-m)\,\omega^2 g(0;\omega)} \qquad (4.26)$$

Using the principal part of $g(0;\omega) = \dfrac{1}{2\pi m}\displaystyle\int_0^{2\pi}\dfrac{dk}{\frac{4\gamma}{m}(1-\cos k)-\omega^2}$

in eqn. (4.26) we get

$$X(t) = \dfrac{m'}{m}\dfrac{X(0)}{\pi}\int_{\omega_L}^{\infty}\dfrac{\sin\omega t\, d\omega}{\lambda\omega + \left(\omega^2-\omega_L^2\right)^{1/2}}, \qquad (4.27)$$

where

$$\lambda = \dfrac{m'-m}{m} \quad\text{and}\quad \omega_L^2 = \dfrac{4\gamma}{m}.$$

For $0 < \lambda < 1$, $\dfrac{1}{\left(\omega^2 - \omega_L^2\right)^{\frac{1}{2}} + \lambda\omega}$ can be expanded as

$$\frac{1}{\sqrt{\omega^2 - \omega_L^2} + \lambda\omega} = \frac{1}{\sqrt{\omega^2 - \omega_L^2} + \omega} \sum_{n=0}^{} \frac{(1-\lambda)^n \omega^n}{\left(\omega + \sqrt{\omega^2 - \omega_L^2}\right)^n} \qquad (4.28)$$

Substituting (4.28) in (4.27) we get

$$X(t) = \frac{m}{m'} \frac{X(0)}{\pi} \sum_{n=0}^{} (1-\lambda)^n I_n(t) \quad , \quad (4.29)$$

where

$$I_n(t) = \frac{\partial^n}{\partial t^n} \left[\frac{1}{\omega_L^{n+1}} \left(\frac{(n+1)\pi}{2t} J_n(\omega_L t) - C_{n+1}\delta_{n,\text{odd}} \right. \right.$$
$$\left. \left. - S_{n+1}\delta_{n,\text{even}} \right) \right]$$

with

$$S_{n+1}(t) = \int_0^{\pi/2} \sin(n+1)\theta \, \sin(\omega_L \sin\theta) \, \omega_L \cos\theta \, d\theta \quad ,$$

$$C_{n+1}(t) = \int_0^{\pi/2} \cos(n+1)\theta \, \cos(\omega_L \sin\theta) \, \omega_L \cos\theta \, d\theta \quad ,$$

and

$J_n(\omega_L t)$ is a Bessel function of the first kind.

This example clearly shows the difficulties involved in determining X(t) explicitly for a general defect.

Takeno and Hori[53] have shown that a very heavy impurity in one-dimensional and three-dimensional lattices behaves like a Brownian particle in the continuum approximation. Recently, Eisenriegler[54] has discussed the dynamics of an isotope defect analytically assuming a spectrum of $\sim \omega^2 \sqrt{\omega_L^2 - \omega^2}$ for the frequencies of the perfect lattice.

§4.4 Dynamics of the Atoms around a Vacancy

Vacancies in a lattice have received particular attention in literature because of the role they play in many physical phenomena and the vast amount of data available on them. However, no exact method of studying the dynamics of a vacancy seems to have been given so far. The model of a vacancy that is generally used is to regard it as a limiting case of a substitutional defect of mass m' and force constant γ' for m' $\rightarrow$ 0 and $\gamma' \rightarrow 0$. Effectively, this defect is known to weaken the force constants considerably. In an alternative model, therefore, vacancy at a lattice site is produced by cutting off the force constants connecting the atom at that site to other atoms; mass of the atom at the vacant site being immaterial.

We shall briefly mention some of the results about vacancies obtained by earlier authors. Lengler and Ludwig[18] have shown that a vacancy in the simple cubic lattice does not have localized modes of vibration. This result has also been reported by Janot and Champier[56].

Land and Goodman[55] have used a molecular model to investigate the possibilities of localized modes at a vacancy. They assume, to begin with, that only one or two shells of atoms around the vacancy can relax and calculate the frequencies of the normal modes. The highest frequency modes obtained from them are then identified as the possible localized modes, the changed frequencies of such modes with increasing number of free shells

around the vacancy are then calculated. Land and Goodman
have proved that the existence of localized modes at a vacant
site depends mainly on the relaxation of structure when the
atom is removed and consequently on the form of interatomic
potential and lattice type. A vacancy, for example, has a
localized mode (with frequency 1% above the continuum) of A_{2u}
symmetry in copper but does not have localized modes in iron
and sodium. Takeno[57] has discussed the vibrations of a diatomic
simple cubic lattice with a hole. He has ignored the changes in
polarizabilities and effective charges of atoms and the vacancy
has been regarded as a change in force constants only, in the first
approximation. Takeno has shown that the vacancy may have
localized modes in the forbidden gap but has no localized modes
outside the optical band.

Krumhansl[22] has shown that lattice vacancies can act as
resonant scatterers at frequencies well below the Debye
frequencies. Such a resonance scattering has been observed
experimentally by Schwartz and Walker[58]. They have measured
the thermal conductivity of alkali halides doped with divalent
impurities. Schwartz and Walker have interpreted the dip in
the thermal conductivity curve as mainly due to the phonon
resonance as it is found that the position of dip is independent
of the mass of the divalent ion and its agreement with the
theoretical results of Krumhansl[22] requires practically no
force constant for the scattering centres.

§ 4.4a   Vibrational Modes of a Vacancy in the Square Lattice.

A vacancy is created at the origin of subspace Γ_2 by cutting off the force constants connecting the atom 0 to its four nearest neighbours labelled as 1 to 4 (figure (1a)). The atoms (1-4) constitute the pseudomolecule. In the scalar model, the displacement vector $\underline{X}_2'(t)$ of the pseudomolecule is,

$$\underline{X}_2'(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \\ x_4(t) \end{pmatrix}, \qquad (4.30)$$

where $x_n(t)$ is displacement of the nth atom from its equilibrium position.

The unitary matrix $\hat{S}$ representing a transformation to the normal co-ordinates of the pseudomolecule is given as

$$\hat{S} = \begin{pmatrix} 1/2 & 1/2 & 1/\sqrt{2} & 0 \\ 1/2 & -1/2 & 0 & 1/\sqrt{2} \\ 1/2 & 1/2 & -1/\sqrt{2} & 0 \\ 1/2 & -1/2 & 0 & -1/\sqrt{2} \end{pmatrix} \qquad (4.31)$$

The matrix $\hat{G}_c(\omega)$ is given in Appendix II (§3.4a). Using $\hat{G}_c(\omega)$ and $\hat{C}$ (§3.4a), it can be shown

$$\left(\hat{G}_c^{-1}(\omega) - \hat{C} - \hat{m}\,\omega^2 \right)_c = \begin{pmatrix} D-4\gamma+m\omega^2 & E & F & E \\ E & D-4\gamma+m\omega^2 & E & F \\ F & E & D-4\gamma+m\omega^2 & E \\ E & F & E & D-4\gamma+m\omega^2 \end{pmatrix}$$

$$(4.32)$$

where

$$D = \frac{1}{2}\left[\frac{\gamma}{2}\frac{g_0}{g_1} + \frac{1}{2}(g_0+g_2-2g_{11})^{-1} + (g_0-g_2)^{-1}\right] \quad,$$

$$E = \frac{1}{2}\left[\frac{\gamma}{2}\frac{g_0}{g_1} - \frac{1}{2}(g_0+g_2-2g_{11})^{-1}\right] \quad,$$

$$(4.33)$$

$$\text{and } F = \frac{1}{2}\left[\frac{\gamma}{2}\frac{g_0}{g_1} + \frac{1}{2}(g_0+g_2-2g_{11})^{-1} - (g_0-g_2)^{-1}\right] \quad.$$

The spectral density matrix of normal modes of the vacancy
is

$$\hat{J}(\omega) = \frac{im\omega}{2\pi}\begin{pmatrix} \gamma(\frac{g_0}{g_1}-1) & 0 & 0 & 0 \\ 0 & (g_0+g_2-2g_{11})^{-1}-\gamma & 0 & 0 \\ 0 & 0 & (g_0-g_2)^{-1}-\gamma & 0 \\ 0 & 0 & 0 & (g_0-g_2)^{-1}-\gamma \end{pmatrix}^{-1}$$

$$(4.34)$$

From the discussion of §4.2 and eqn. (4.34) it follows that
the frequencies of persistent modes, if present, are given
by solutions of the following equations (the equations for
$\omega^2 < \omega_L^2$ arise by equating the real parts of basic equations
to zero to look for possible resonances).

(i)   Mode $(1,1,1,1)$: $g_0 = g_1$ (4.35)

Substituting the analytic forms of the Green functions[3]
and the sum-rules satisfied by Green functions (eqns. (3.9)
and (3.10)), eqn. (4.35) gives the following conditions:

$$K(\eta) = -\frac{\pi}{2}\left(\frac{1}{1-\eta}\right) \quad, \qquad 0 < \omega^2 < \frac{1}{2}\omega_L^2 \qquad (4.36a)$$

$$F(\eta') = \frac{\pi}{2}\left(\frac{1}{1+\eta'}\right), \qquad \frac{\omega_L^2}{2} < \omega^2 < \omega_L^2 \qquad (4.36b)$$

$$K(\rho) = \frac{\pi}{2}\left(\frac{1}{1+\rho}\right), \qquad \omega^2 > \omega_L^2 \qquad (4.36c)$$

where

$$\eta = \frac{4\gamma - m\omega^2}{4\gamma}, \qquad \eta' = \frac{m\omega^2 - 4\gamma}{4\gamma},$$

$$\rho = \frac{4\gamma}{m\omega^2 - 4}, \qquad \omega_L^2 = \frac{8\gamma}{m},$$

and K's are the complete elliptic integrals of the first kind. None of the equations (4.36a-4.36c) has a solution (Figure 3a).

(ii) Mode $(1, \bar{1}, 1, \bar{1})$: $g_0 + g_2 - 2g_{11} = \frac{1}{\gamma}$ (4.37)

Eqn. (4.37) yields

$$(1 - \eta^2)K(\eta) = 2E(\eta) - \frac{\pi}{2}(1+\eta), \qquad 0 < \omega^2 < \frac{1}{2}\omega_L^2 \qquad (4.37a)$$

$$(1 - \eta'^2)K(\eta') = 2E(\eta') + \frac{\pi}{2}(1-\eta'), \qquad \frac{\omega_L^2}{2} < \omega^2 < \omega_L^2 \qquad (4.37b)$$

$$(1 - \rho^2)K(\rho) = 2E(\rho) - \frac{\pi}{2}(1-\rho), \qquad \omega^2 > \omega_L^2 \qquad (4.37c)$$

where E's are the complete elliptic integrals of second kind. Eqns. (4.37a-4.37c) do not have any solutions (Figure 3b) showing thereby that $(1,\bar{1},1,\bar{1})$ is not a persistent mode.

(iii) The doubly-degenerate mode $(1,0,\bar{1},0)$ and $(0,1,0,1)$: $g_0 - g_2 = 1/\gamma$

$$(4.38)$$

Eqn. (4.38) leads to

$$(1 - \eta^2)K(\eta) = E(\eta) + \frac{\pi}{2}(1-\eta), \qquad 0 < \omega^2 < \frac{\omega_L^2}{2} \qquad (4.38a)$$

$$(1 - \eta'^2)K(\eta') = E(\eta') - \frac{\pi}{2}(1+\eta'), \qquad \frac{\omega_L^2}{2} < \omega^2 < \omega_L^2 \qquad (4.38b)$$

$$E(\rho) = \frac{\pi}{2}(1+\rho) \qquad \omega^2 < \omega_L^2 \qquad (4.38c)$$
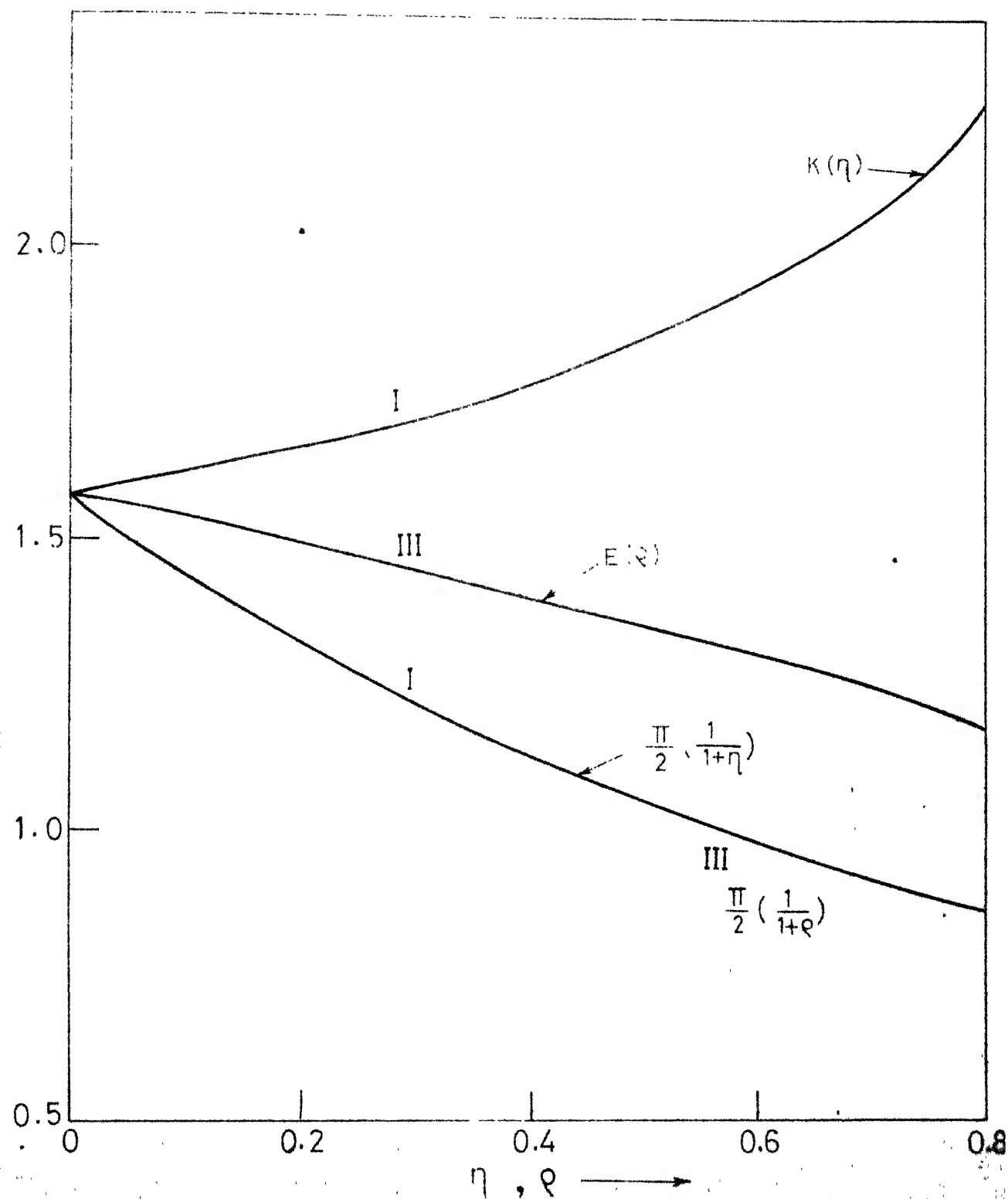
Fig. 3a   Plots for the solution of I Eqns (4.36 b - 4.36 c)
III Eqn (4.38 c)
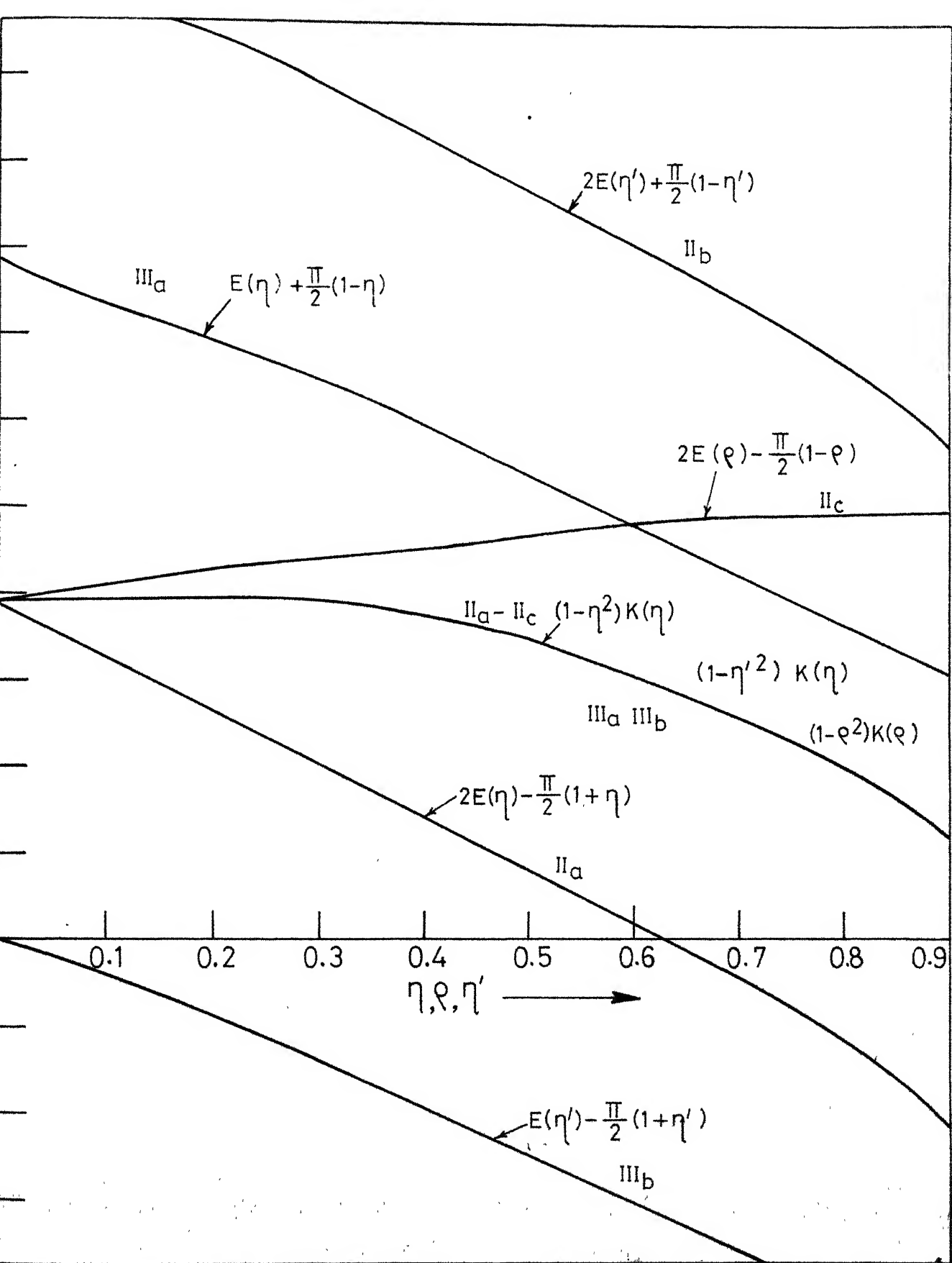
Fig. 3b Graphical solutions of Eqns (4.37a – 4.37c) II_a–II_c and Eqns (4.38a – 4.38b) III_a–III_b.

Eqns. (4.38a-4.38c) also have no solutions (Figures 3a & 3b)
Thus we conclude that a vacancy in the square lattice can
have only relaxing normal vibrational modes.

§4.4b Vacancy in the Simple Cubic Lattice

The model used here is the same as that discussed
in Chapter III. The displacement vector of the pseudo-
molecular atoms is (Figure 2) ,

$$\underline{X}_2'(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \\ x_4(t) \\ x_5(t) \\ x_6(t) \end{pmatrix} , \qquad (4.39)$$

where $x_n(t)$ is the displacement of nth atom.

The matrix representing transformation to the normal coordinat
is given by

$$\hat{S} = \begin{pmatrix} 1/\sqrt{6} & 1/\sqrt{2} & 0 & 0 & 1/\sqrt{12} & 1/2 \\ 1/\sqrt{6} & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{12} & -1/2 \\ 1/\sqrt{6} & 0 & 0 & 1/\sqrt{2} & -2/\sqrt{12} & 0 \\ 1/\sqrt{6} & -1/\sqrt{2} & 0 & 0 & 1/\sqrt{12} & 1/2 \\ 1/\sqrt{6} & 0 & -1/\sqrt{2} & 0 & 1/\sqrt{12} & -1/2 \\ 1/\sqrt{6} & 0 & 0 & -1/\sqrt{2} & -2/\sqrt{12} & 0 \end{pmatrix}$$

$$(4.40)$$

The labels of the rows and columns of $\hat{S}$ in eqn. (4.40)
are   in the order of indices of atoms 1-6.

The form of spectral density matrix $\hat{J}(\omega)$ is given
by

$$\hat{J}(\omega) = \frac{im\omega}{2\pi} \begin{pmatrix} (\frac{g_0}{g_1}-1)\gamma & 0 & 0 & 0 & 0 & 0 \\ 0 & (g_0-g_2)^{-1} & 0 & 0 & 0 & 0 \\ & & -\gamma & & & \\ 0 & 0 & (g_0-g_2)^{-1} & 0 & 0 & 0 \\ & & -\gamma & & & \\ 0 & 0 & 0 & (g_0-g_2)^{-1} & 0 & 0 \\ & & & -\gamma & & \\ 0 & 0 & 0 & 0 & (g_0+g_2 & 0 \\ & & & & -2g_3)^{-1} & \\ & & & & -\gamma & \\ 0 & 0 & 0 & 0 & 0 & (g_0+g_2 \\ & & & & & -2g_3)^{-1} \\ & & & & & -\gamma \end{pmatrix}$$

$$(4.41)$$

with $g(\underline{l},\underline{l'};\omega) \equiv g(l_1-l'_1, l_2-l'_2, l_3-l'_3;\omega)$,

$g_0 = g(0,0,0;\omega)$, $g_1 = g(1,0,0;\omega)$; $g_2 = g(2,0,0;\omega)$
and $g_3 = g(1,1,0;\omega)$ and these elements of the Green functions
are as defined by eqn. (3.21).

The conditions for existence of the persistent modes are,

(1) Mode $(1,1,1,1,1,1)$: $g_0 = g_1$ (4.42)

(2) Mode $(1,0,0,\bar{1},0,0)$: $g_0-g_2 = 1/\gamma$ (4.43)

(3) Doubly-degenerate mode $(0,1,0,0,\bar{1},0);(0,0,1,0,0,\bar{1})$:

$$g_0 + g_2 - 2g_3 = 1/\gamma \quad (4.44)$$

To find the solution of these equations the required
Green functions have to be computed numerically. The method
of Fourier-Series expansion[30] (viz. the imaginary part of a
Green function is expressible as a Fourier sine-series with
some Bessel functions as coefficients) has been used for the
same. It is found that only the mode $(1,1,1,1,1,1)$ has a
solution which is a rather broad resonance at $\omega^2 = 0.8\,\omega_L^2$
(Fig. 4). The other two equations (4.43) and (4.44) do not
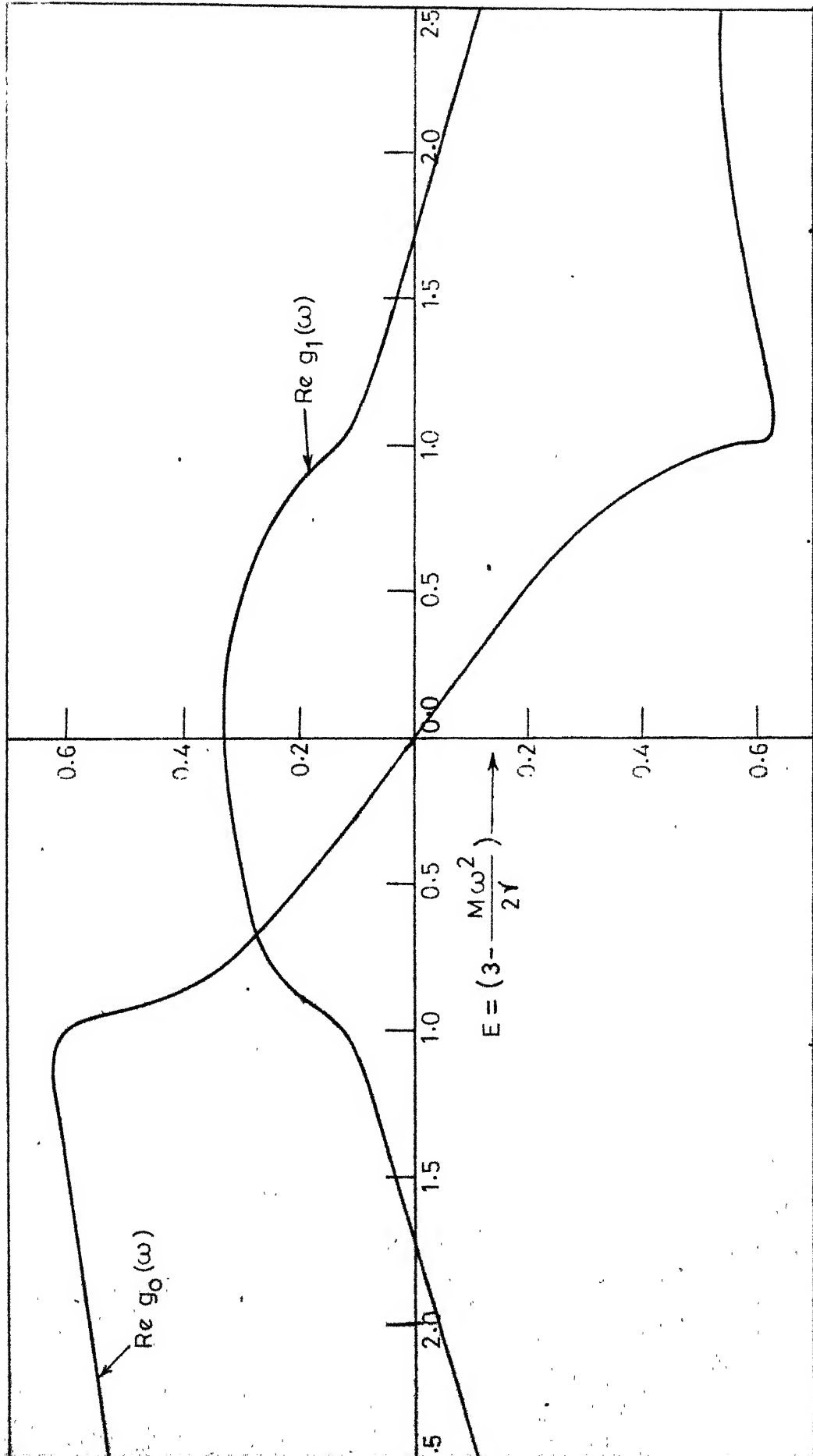
Fig. 4 Resonance mode of a vacancy in the simple cubic lattice: Root of Eqn Re $g_0(\omega) =$ Re $g_1(\omega)$.

have any solutions and therefore correspond to relaxing modes of vibration. Thus a vacancy in the simple cubic lattice does not have localized modes of vibration.

The result that a vacancy does not have localized vibrational modes is understandable on the basis of a substantial amount of weakening of the force constants caused by it. By Rayleigh's theorem[23] the frequencies of such a defect should decrease. However, relaxation around the vacant site may adjust the force constants such that it shows localized modes, as has been discussed by Land and Goodman[55]. Many authors have given methods of finding relaxation around the defects in cubic lattices. In more detailed calculations, relaxation due to defects can be taken into account by choosing a bigger pseudomolecule.

4.5 Correlation Functions Associated with a Point Defect

The formalism of §4.1 and §4.2 shall be used in this section to give a method of computing the correlation functions associated with a general point defect which are required for calculations of Mössbauer line-width, neutron scattering cross-section, optical absorption, transport Coefficients etc.[4,5,51].

The time-dependent correlation functions of displacements and velocities of atoms in the imperfect crystal are defined as[59],

$$\langle x_\alpha(l;t) x_\beta(l' \neq 0)\rangle = \frac{\hbar}{\pi} \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t) \frac{\text{Sgn } \omega}{\exp(-\beta\hbar\omega)-1}$$

$$\text{Im } G'_{\alpha\beta}(l,l';\omega^2-i\epsilon) \quad \epsilon \longrightarrow 0 \qquad (4.45)$$

$$\langle p_\alpha(l;t) p_\beta(l';0)\rangle = \frac{\hbar}{\pi} M_l M_{l'} \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t) \frac{\omega^2 \text{Sgn } \omega}{\exp(-\beta\hbar\omega)-1}$$

$$\text{Im } G'_{\alpha\beta}(\underline{l},\underline{l}';\omega^2-i\epsilon) \qquad (4.46)$$

$$\langle x_\alpha(\underline{l};t) p_\beta(\underline{l}';0)\rangle = \frac{i\hbar}{\pi} M_{l'} \int_{\underline{}}^{+} d\omega \exp(-i\omega t) \frac{\omega \text{ Sgn } \omega}{\exp(-\beta\hbar\omega)-1}$$

$$\text{Im } G'_{\alpha\beta}(\underline{l},\underline{l}';\omega^2-i\epsilon), \qquad (4.47)$$

where $\langle \ldots \rangle$ denotes the thermal average; $\beta = 1/k_B T$, k_B being the Boltzmann's constant and T is the temperature. $\hat{G}'$, the Green functions matrix of the imperfect crystal, is defined as

$$\hat{G}' = (\hat{L}' - \hat{M}'\omega^2)^{-1} \qquad (4.48)$$

where $\hat{L}'$ and $\hat{M}'$ are matrices of the atomic force constants and masses, respectively.

For correlation functions associated with a point defect, $\underline{l}$ and $\underline{l}'$ in eqns. (4.45)-(4.47) are to be restricted over the indices of pseudomolecular coordinates. Therefore $\hat{G}'$ in these equations can be replaced by the submatrix $\hat{G}'_c$ which can be written in terms of $\hat{G}_c$ and parameters of the defect by using eqns. (2.9) and (2.15). Hence eqns. (4.45)-(4.47) can be rewritten as,

$$\langle x_\alpha(\underline{l};t) x_\beta(\underline{l}';0)\rangle = \frac{\hbar}{\pi} \int_{\underline{}}^{+} d\omega\, e^{-i\omega t} \frac{\text{Sgn } \omega}{\exp(-\beta\hbar\omega)-1}$$

$$\text{Im}\left[\hat{m}'\omega^2 - \hat{C}' + \left(\hat{G}_c^{-1} + \hat{C} - \hat{m}\omega^2 \right)_{c,a} \right]^{-1} \qquad (4.45a)$$

$$\langle p_\alpha(\underline{\ell};t)\, p_\beta(\underline{\ell}';0)\rangle = \frac{\hbar}{\pi} M_\ell M_{\ell'} \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, \frac{\omega^2 \operatorname{Sgn}\omega}{e^{-\beta\hbar\omega}-1} \times$$

$$\operatorname{Im}\left[\hat{m}'\,\omega^2-\hat{C}' +(\hat{G}_C^{-1}+\hat{C}-\hat{m}\,\omega^2)_{c,a}\right]^{-1} \quad (4.46a)$$

$$\langle x_\alpha(\underline{\ell};t)\, p_\beta(\underline{\ell}';0)\rangle = \frac{i\hbar}{\pi} M_{\ell'} \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, \frac{\omega \operatorname{Sgn}\omega}{e^{-\beta\hbar\omega}-1}$$

$$\operatorname{Im}\left[\hat{m}'\,\omega^2-\hat{C}' +(\hat{G}_C^{-1}+\hat{C}-\hat{m}\,\omega^2)_{c,a}\right]^{-1} \quad (4.47a)$$

Mansel et al.[60] have studied the Debye-Waller factor of the Mossbauer isotope Au^{197} obtained by irradiating platinum wi neutrons. They have concluded that the Debye Waller factor dro appreciably when the Mössbauer atom is nearest to a close Frenk pair. As an example, therefore, we shall obtain here an express for the Debye Waller factor, f, of one of the nearest neighbour of a vacancy in the isotropic simple cubic lattice (model consi ed here is the same as that used in §4.4b). f is defined as[5]

$$f = \exp(-2K\langle x^2(10)\rangle) \quad (4.48)$$

$\langle x^2(10)\rangle$ is obtained from eqn. (4.45a) by putting $t = 0$

$$\langle x^2(10)\rangle = \frac{\hbar}{\pi} \int_0^\infty d\omega \operatorname{Coth}(\beta\hbar\omega/2) \operatorname{Im} G_C'(10,10;\omega^2-i\epsilon) \quad (4.49)$$

Using the matrices required in eqn. (4.49) from those given in §4.4b we get

$$\operatorname{Im} G_C'(10;10;\omega^2-i\epsilon) = \frac{1}{6} \operatorname{Im}\left[\frac{g_0}{(g_0-g_1)} + \frac{2(g_0+g_2-2g_3)}{1-\gamma(g_0+g_2-2g_2)}\right.$$

$$\left. + \frac{3(g_0-g_2)}{1-\gamma(g_0-g_2)}\right] \quad (4.50$$

Imaginary parts of the various terms occurring in eqn. (4.50) can be simplified as,

$$\text{Im } \frac{g_o - g_2}{1 - \gamma(g_o - g_2)} = \frac{1}{\gamma} \text{ Im}\left[\frac{1}{1 - \gamma(g_o - g_2)}\right]$$

$$= \frac{\text{Im}(g_o - g_2)}{(1 - \gamma \text{Re}(g_o - g_2))^2 + (\text{Im}(g_o - g_2))^2}$$

$$(4.51)$$

The required Greens functions can be computed numerically[30].

We have not computed any numerical results here. Lakatos and Krumhansl[61] have given analytic expressions for the mean square displacement of the impurity and its nearest neighbours in f.c.c. and b.c.c. lattices. Goldman[62] and, Haridasan and Nandini[63] have reported calculation of Debye-Waller factor in rare gas solids and cesium-halides. Calculations and precision measurements of Mössbauer fraction of Fe^{57} impurity in Pt, Pd and Cu have been reported, respectively, by Patnaik and Mahanty[64] and Nussbaum et al.[6

CHAPTER V

PSEUDOMOLECULAR MODEL FOR A SUBSTITUTIONAL IMPURITY
IN A LATTICE OF POLARISABLE ATOMS

§5.1 Introduction

In the calculations based on pseudomolecular model
in the previous chapters, the atoms were regarded as non-
polarizable. The usefulness of the shell-model treatment
of lattice vibrations has been amply demonstrated by
now[66,67]. In this model, as proposed originally by Dick
and Overhauser[68], each atom is regarded as consisting of
a core surrounded by a massless shell composed of some of
the outermost electrons. The cores and shells are assumed
to be connected by certain short-range force constants.
Under the influence of these short-range forces, each atom
has a distortion polarisability in addition to the polar-
izability induced by the electric fields. The potential
energy for such a model, in the harmonic approximation, is
expressible as a quadratic in the core-displacements and
electronic dipole moments. In this chapter we shall cons-
ider a pseudomolecular model for a substitutional defect
which does not change the long-range Coulomb forces due
to the charges of shells and cores.

In the notation of Cowley et al.[69], the equations
of motion of the lattice in the shell-model can be
written as,

$$\begin{pmatrix} \hat{\Phi}_{cc} - \hat{M}_c \omega^2 & \hat{\Phi}_{cs} \\ \hat{\Phi}_{cs}^T & \hat{\Phi}_{ss} \end{pmatrix} \begin{pmatrix} \underline{U} \\ \underline{V} \end{pmatrix} = 0 , \qquad (5.1)$$

where $\underline{U}$ and $\underline{V}$ denote the displacements of the cores and shells, respectively, from their equilibrium positions. $\hat{\Phi}_{cc}$, $\hat{\Phi}_{cs}$ and $\hat{\Phi}_{ss}$ are matrices of the force constants between cores and cores, cores and shells and between shells and shells, respectively. Each of these $\hat{\Phi}$ matrices consists of a short range part $\hat{\Phi}^R$ and a long-range part (arising from the Coulomb forces) such that[69],

$$\hat{\Phi}_{cc} = \hat{\Phi}_{cc}^R + \hat{X} \hat{C} \hat{X} ; \quad \hat{\Phi}_{cs} = \hat{\Phi}_{cs}^R + \hat{X} \hat{C} \hat{Y}$$

$$(5.2)$$

and

$$\hat{\Phi}_{ss} = \hat{\Phi}_{ss}^R + \hat{Y} \hat{C} \hat{Y} ,$$

where $\hat{X}$ and $\hat{Y}$ are diagonal matrices of the core and shell charges, respectively. $\hat{C}$ is a matrix of the Coulomb coefficients.

Eliminating $\underline{V}$ from equations (1) we get

$$(\hat{\Phi}_{cc} - \hat{\Phi}_{cs} \hat{\Phi}_{ss}^{-1} \hat{\Phi}_{cs}^T)\underline{U} = 0 \qquad (5.3)$$

As discussed by Lax[70], $\hat{\Phi}_{cs}^R \hat{\Phi}_{ss}^{R^{-1}} \tilde{\Phi}_{cs}^R$ is a long-range term due to the occurrence of $(\hat{\Phi}_{ss}^R)^{-1}$ in it. Though, in principle, eqn. (3) can be partitioned in the same way as done in Chapter II, this is of no special advantage here as the long-range nature of $\hat{\Phi}_{cs} \hat{\Phi}_{ss}^{-1} \hat{\Phi}_{cs}^T$ makes it cumbersome to take into account changes in the shell parameters at the

point defect.   We shall show here that if the core and shell coordinates are taken together to form the pseudo-molecule and if the long-range Coulomb terms in eqns. (5.2) and (5.3) are assumed to remain unchanged, a local effective interaction term can be obtained in terms of the defect parameters.

5.2   Pseudomolecular Model

We partition $\left|\dfrac{U}{V}\right|$ and the matrix of force constants in eqn. (1) as follows

$$\left(\frac{U}{V}\right) = \left|\begin{array}{c} \dfrac{U_1}{U_2} \\ \dfrac{V_1}{V_2} \end{array}\right| \tag{5.4}$$

$$\hat{\Phi} = \begin{array}{c} \\ n_1 \\ n_2 \\ n_1 \\ n_2 \end{array} \begin{array}{cccc} n_1 & n_2 & n_1 & n_2 \\ (\hat{\Phi}_{cc} - \omega^2 \hat{M}_c)_{11} & (\hat{\Phi}_{cc} - \omega^2 \hat{M}_c)_{12} & (\hat{\Phi}_{cs})_{11} & (\hat{\Phi}_{cs})_{12} \\ (\hat{\Phi}_{cc} - \omega^2 \hat{M}_c)_{21} & (\hat{\Phi}_{cc} - \omega^2 \hat{M}_c)_{22} & (\hat{\Phi}_{cs})_{21} & (\hat{\Phi}_{cs})_{22} \\ (\hat{\Phi}_{cs}^T)_{11} & (\hat{\Phi}_{cs}^T)_{12} & (\hat{\Phi}_{ss})_{11} & (\hat{\Phi}_{ss})_{12} \\ (\hat{\Phi}_{cs}^T)_{21} & (\hat{\Phi}_{cs}^T)_{22} & (\hat{\Phi}_{ss})_{21} & (\hat{\Phi}_{ss})_{22} \end{array}$$

$$\tag{5.5}$$

where 1 and 2 refer to indices of regions I and II of the crystal. n_1 and n_2 are degrees of freedom associated with regions I and II, respectively.   The dimensions of the submatrices of $\hat{\Phi}$ in eqn. (5.5) are as indicated by n's.

We define a unitary transformation matrix $\hat{S}$ as follows:

$$
\hat{S} = \begin{array}{c} \\ n_1 \\ \\ n_1 \\ \\ n_2 \\ \\ n_2 \end{array}
\begin{array}{cccc} n_1 & n_2 & n_1 & n_2 \\ \left(\hat{I} \right. & O & O & O \\ O & O & \hat{I} & O \\ O & \hat{I} & O & O \\ O & O & O & \left. \hat{I} \right) \end{array}
\qquad (5.6)
$$

Applying the transformation $\hat{S}$ to eqn. (5.1), with the displacement vector and matrix of force constants partitioned as shown by eqns. (5.4) and (5.5), we get

$$
\hat{\underline{\Phi}}_s \underline{\chi} = 0 , \qquad (5.7)
$$

where

$$
\hat{\underline{\Phi}}_s = \hat{S} \, \hat{\underline{\Phi}} \, \hat{S}^{-1} , \qquad (5.8)
$$

and

$$
\underline{\chi} = \begin{pmatrix} \underline{\chi}_1 \\ \underline{\chi}_2 \end{pmatrix} \quad \text{with} \quad \underline{\chi}_1 = \begin{pmatrix} \underline{U}_1 \\ \underline{V}_1 \end{pmatrix} \text{ and } \quad \underline{\chi}_2 = \begin{pmatrix} \underline{U}_2 \\ \underline{V}_2 \end{pmatrix} \qquad (5.9)
$$

From eqns. (5.7) and (5.9), eqn. for $\underline{\chi}_2$ can be written as

$$
(\hat{\underline{\Phi}}_{22}^s - \widetilde{\underline{\Phi}}_{12}^s \, \hat{\underline{\Phi}}_{11}^{s-1} \, \hat{\underline{\Phi}}_{12}^s) \, \underline{\chi}_2 = 0 \quad , \qquad (5.10)
$$

or

$$
\hat{G}_c^{-1} \, \underline{\chi}_2 = 0 . \qquad (5.11)
$$

where

$$\hat{\Phi}_s = \begin{pmatrix} \hat{\Phi}_{11}^s & \hat{\Phi}_{12}^s \\ \hat{\Psi}_{12}^s & \hat{\Psi}_{22}^s \end{pmatrix} \quad \text{and} \quad \hat{G}_s = \hat{\Phi}_s^{-1} = \begin{pmatrix} \hat{G}_A & \hat{G}_B \\ \hat{G}_B^T & \hat{G}_C \end{pmatrix} \quad (5.12)$$

From eqn. (5.8)

$$\hat{G}_s = \hat{\Phi}_s^{-1} = \hat{S}\,\hat{\Phi}^{-1}\,\hat{S}^{-1} = \hat{S}\,\hat{G}\,\hat{S}^{-1} \quad (5.13)$$

and

$$\hat{G} = \hat{\Phi}^{-1} = \begin{pmatrix} \hat{\Phi}_{cc} - \omega^2\hat{M}_2 & \hat{\Phi}_{cs} \\ \hat{\Phi}_{cs}^T & \hat{\Phi}_{ss} \end{pmatrix}^{-1} = \begin{pmatrix} \hat{G}_{cc} & \hat{G}_{cs} \\ \hat{G}_{cs}^T & \hat{G}_{ss} \end{pmatrix} \quad (5.14)$$

The required submatrix $\hat{G}_c$ in eqn. (5.11) can be shown, from eqns. (5.13) and (5.14), to be obtainable from the submatrices of $\hat{G}$ as follows:

$$\hat{G}_c = \begin{pmatrix} (\hat{G}_{cc})_{22} & (\hat{G}_{cs})_{22} \\ (\hat{G}_{cs}^T)_{22} & (\hat{G}_{ss})_{22} \end{pmatrix} \quad , \quad (5.15)$$

where indices in the submatrices of $\hat{G}_c$ are restricted to those of region II only.

The matrix of Green functions, defined by eqn. (5.14), can be written as

$$\hat{G}_{cc}(\underline{R},\underline{R}';\omega) = \frac{1}{2\pi}\int_0^{2\pi} d\underline{k}\; e^{-i\underline{k}\cdot(\underline{R}'-\underline{R})}\frac{\hat{D}_{ss}(\underline{k})}{\hat{D}_{cc}(\underline{k})\,\hat{D}_{ss}(\underline{k}) - \hat{D}_{cs}(\underline{k})\,\hat{D}_{cs}(\underline{k})} \quad ,$$

$$(5.16)$$

$$\hat{G}_{cs}(R,\underline{R}';\omega) = \frac{1}{2\pi} \int_0^{2\pi} d\underline{k} \; e^{-i\underline{k}\cdot(\underline{R}'-\underline{R})} \frac{\hat{D}_{cs}(\underline{k})}{\hat{D}_{cc}(\underline{k})\,\hat{D}_{ss}(\underline{k}) - \hat{D}_{cs}(\underline{k})\,\hat{D}_{cs}(\underline{k})}$$

$$(5.17)$$

$$\hat{G}_{ss}(\hat{\underline{R}},\hat{\underline{R}}';\omega) = \frac{1}{2\pi} \int_0^{2\pi} d\underline{k} \; e^{-i\underline{k}\cdot(\underline{R}'-\underline{R})} \cdot \frac{\hat{D}_{cc}(k)}{\hat{D}_{cc}(k)\hat{D}_{ss}(k) - \hat{D}_{cs}(k)\hat{D}_{cs}(k)}$$

$$(5.18)$$

where

$$\hat{D}_{ss}(\underline{k}) = \sum_{R'} \hat{\tilde{\Phi}}_{ss}(\underline{R},\underline{R}') \; e^{i\underline{k}\cdot(\underline{R}'-\underline{R})},$$

$$\hat{D}_{cs}(\underline{k}) = \sum_{R'} \hat{\tilde{\Phi}}_{cs}(\underline{R},\underline{R}') \; e^{i\underline{k}\cdot(\underline{R}'-\underline{R})}, \qquad (5.19)$$

and

$$\hat{D}_{cc}(\underline{k}) = \sum_{R'} (\hat{\tilde{\Phi}}_{cc} - \omega^2 \hat{M}_c)_{\underline{R},\underline{R}'} \; e^{i\underline{k}\cdot(\underline{R}'-\underline{R})}.$$

We shall consider here only those substitutional impurities which do not change the number of degrees of freedom associated with the lattice and only the core and shell parameters of the atom replaced by the impurity are affected. The matrix $\hat{C}$ in eqn. (5.2) is also assumed to remain unchanged. The formalism so developed may be useful in many physical situations (e.g., for defects like Li^+ and K^+ in NaI crystals which have been treated as essentially mass defects[71]). For such defects, the submatrices $\hat{\tilde{\Phi}}_{12}^s$, $\hat{\Phi}_{11}^s$ and $\tilde{\tilde{\Phi}}_{12}^s$ of $\hat{\Phi}^s$ (eqn. 5.12) remain unaltered if the pseudomolecule (i.e., Γ_2) is chosen such that the short-range shell parameters between

the peripheral atoms of the pseudomolecule and those of the unperturbed region I do not change. The change in matrix $\hat{\Phi}^{s}_{22}$ due to the defect can be determined in terms of the shell-parameters of the perturbed region II only.

The equation of motion of the imperfect pseudomolecule can therefore be written from eqn. (5.10) as,

$$(\hat{\Phi}^{s\prime}_{22} - \hat{\Phi}^{s}_{22} + \hat{G}^{-1}_{c}) \underline{\chi}^{\prime}_{2} = 0, \tag{5.20}$$

where prime denotes the perturbed matrix.

5.3 Application to Simple Cubic Lattice

As an illustrative example we shall obtain here the form of the perturbation matrix $\hat{\Phi}^{s\prime}_{22} - \hat{\Phi}^{s}_{22}$ for a substitutional impurity in the isotropic simple cubic lattice. In the nearest neighbours interaction approximation, $\hat{\Phi}^{s}_{22}$ and $\hat{\Phi}^{s\prime}_{22}$ are (14x14) matrices. Various shell parameters between any two neighbouring atoms of the perfect lattice are as depicted in Fig. (5).
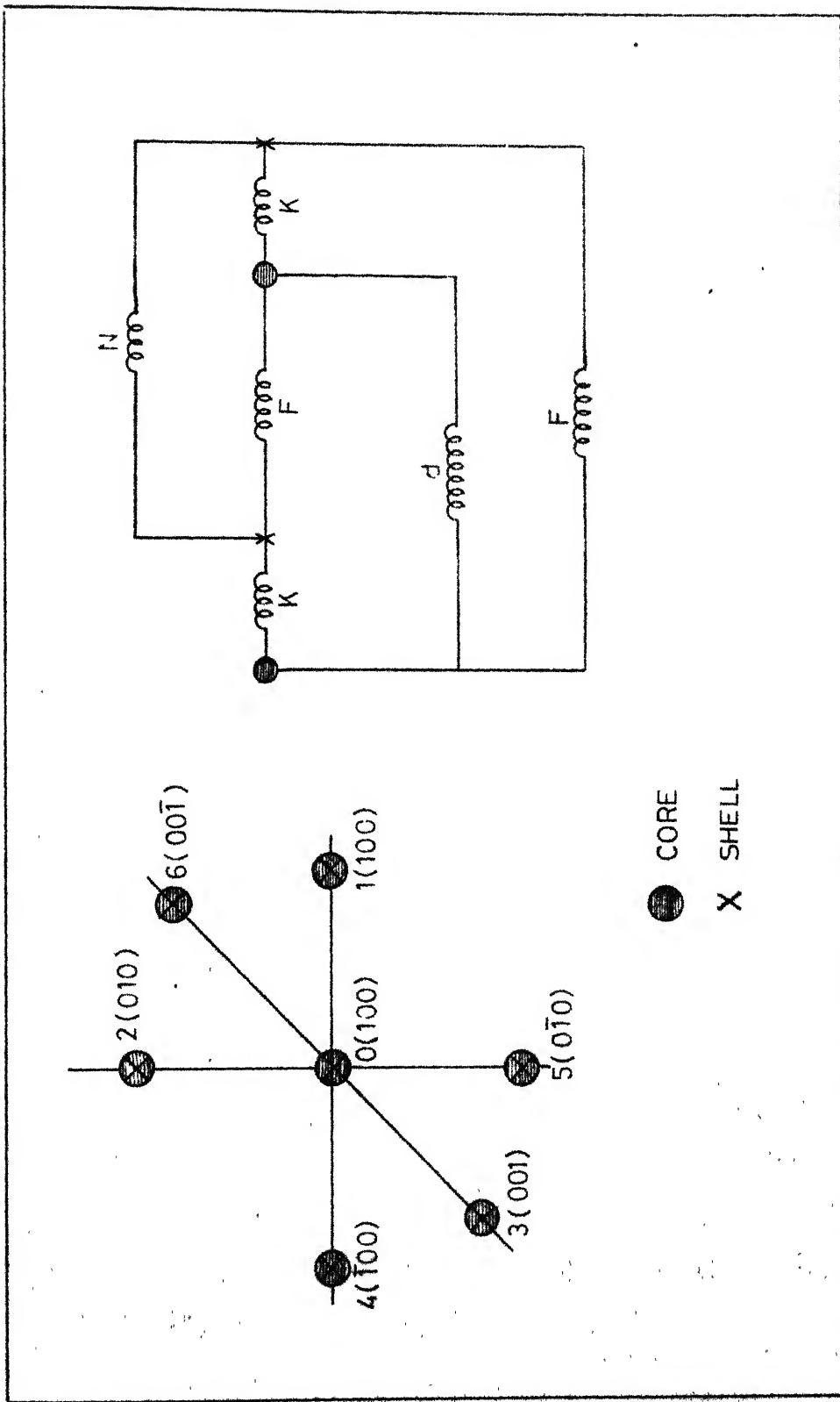
Fig. 5 Shell model parameters for the perfect simple cubic lattice (§ 5.3).

Time-independent equations of motion of the core and shell of the nth atom can be written as,

$$-M_c\,\omega^2 U_n = d\left(\sum_{\substack{i=\text{nearest}\\ \text{neighbours}\\ \text{of } n}} U_i - 6U_n\right) + F\left(\sum_{\substack{i=\text{nearest}\\ \text{neighbours}\\ \text{of } n}} V_i - 6U_n\right) + K(V_n - U_n), \qquad (5.21)$$

$$O = N\left(\sum_{\substack{i=\text{nearest}\\ \text{neighbours}\\ \text{of } n}} V_i - 6V_n\right) + K(U_n - V_n) + F\left(\sum_{\substack{i=\text{nearest}\\ \text{neighbours}\\ \text{of } n}} U_i - 6V_n\right), \qquad (5.22)$$

where M_c is the mass of the core of the nth atom and shells are assumed to be massless.

Matrices $\hat{\Phi}^R_{cc}$, $\hat{\Phi}^R_{cs}$ and $\hat{\Phi}^R_{ss}$ defined by eqns. (5.1) and (5.2) can be obtained from eqns. (5.21) and (5.22) written in matrix form. Using them in eqns. (5.8) and (5.12), matrix $\hat{\Phi}^s_{22}$ can be obtained. Similarly, $\hat{\Phi}^{s'}_{22}$ matrix can be obtained by writing the equations of motion for the imperfect crystals. The explicit form of $\hat{\Phi}^{s'}_{22} - \hat{\Phi}^s_{22}$ in terms of the changes ΔN, ΔF, Δd and ΔK in the shell model parameters due to the impurity is given in Appendix VI .

The procedure for obtaining the spectral density function associated with each mode is similar to that given in § 4.3. The eigen-value equation obtained for the doubly-degenerate E_g-modes $(011\bar{2}\ 11\bar{2}\ 0000000)$ and $(0000000\ 11\bar{2}\ 11\bar{2})$, for example, is

$$
\left(
\begin{array}{cc}
\Delta d + \Delta F + \dfrac{G_{ss}(0)-2G_{ss}(3)+G_{ss}(2)}{|\hat{V}^{+}\hat{G}_{c}\hat{V}|_{E_g}} & \dfrac{G_{cs}(0)-2G_{cs}(3)+G_{cs}(2)}{|\hat{V}^{+}\hat{G}_{c}\hat{V}|_{E_g}} \\[4ex]
\dfrac{G_{sc}(0)-2G_{sc}(3)+G_{sc}(2)}{|\hat{V}^{+}\hat{G}_{c}\hat{V}|_{E_g}} & \Delta N + \Delta F + \dfrac{G_{cc}(0)-2G_{cc}(3)+G_{cc}(2)}{|\hat{V}^{+}\hat{G}_{c}\hat{V}|_{E_g}}
\end{array}
\right) \times
$$

$$
\left(
\begin{array}{c}
u_1 + u_2 - 2u_3 + u_4 + u_5 - 2u_6 \\
v_1 + v_2 - 2v_3 + v_4 + v_5 - 2v_6
\end{array}
\right) = 0 \tag{5.23}
$$

where

$$
|\hat{V}^{+}\hat{G}_{c}\hat{V}|_{E_g} = (G_{cc}(0)-2G_{cc}(3)+G_{cc}(2))(G_{ss}(0)-2G_{ss}(3)+G_{ss}(2))
$$

$$
- (G_{sc}(0)-2G_{sc}(3)G_{sc}(2))(G_{cs}(0)-2G_{cs}(3)+G_{cs}(2)), \tag{5.24}
$$

and

$$
G(\underline{R},\underline{R}') = G(\underline{R}-\underline{R}') = G(R_1-R_1',\ R_2-R_2',\ R_3-R_3')
$$
$$
G(3) = G(1,1,0)
$$
$$
G(2) = G(2,0,0) \tag{5.25}
$$
$$
G(0) = G(0,0,0)
$$
$$
G(1) = G(1,0,0)
$$

and these elements of the Green functions are defined by equation (5.16-5.19).

5.4 Conclusion

It may be mentioned here that the formalism in §5.2 is quite similar to that given by Page and Strauch[19] using Lifshitz's approach. Their method enables one to take into account the changes in Coulomb terms due to the

changes in core and shell charges (changes in the Coulomb matrix due to relaxation of the medium around impurity have been neglected) as a local non-zero submatrix in the full perturbation matrix. The dimension of the force constant matrix in their treatment is increased due to an additional (linearly dependent) equation of motion in eqn. (5.1) and calculations of the Green functions are therefore more involved than in the present approach. It has been pointed out recently by Schroder[72] that a 'Breathing shell model', in which the electronic shells are regarded non-rigid, gives a better agreement with the experimental dispersion curves of some alkali halides. The present method and that suggested by Page and Strauch can both be generalised to the 'Breathing shell model'.

CHAPTER VI

CONCLUSION

The pseudomolecular model of a point defect used in this work is a development on the concepts used earlier by some authors[7,8,9,22]. Its applicability to the self-entropy problem has been discussed by Mahanty[10]. The advantage of this method over the earlier exact and approximation methods lies in the fact that it is readily applicable to a general point defect which may involve a change in the number of degrees of freedom associated with the lattice. Also it is an exact method with computational problems not more involved than what is required in conventional methods. This work contains only model calculations for defects in square, simple cubic and b.c.c. lattices. Calculations should be done for point defects in f.c.c. lattices for which a lot of data exists.

Neglecting relaxation of the medium produced by point defects, the pseudomolecular model has been used to study the exact detailed dynamics of general point defects. The method leads to the exact result that a vacancy in the simple cubic lattice has only relaxing vibrational modes. Land and Goodman[55] have pointed out that localized modes of vacancies (in cubic lattices) with frequencies slightly above the continuum are possible if relaxation of the structure is taken into account. Relaxation of the medium can be taken into account by choosing a bigger pseudomolecule.

A sum-rule for the spectral density matrix of the perfect pseudomolecule has been given. Some similar sum-rule for the imperfect pseudomolecule, if possible, may give information about the frequency distribution function of the imperfect crystal.

The phonon-scattering from point defects has not been discussed within the framework of this formalism. Using a slightly different partitioning method the phonon-scattering can be described in terms of the usual t-matrix formalism, as has been discussed in detail by Wagner[9]. The correlation functions associated with a general point defect, required for many physical problems e.g. scattering of particles by the lattice, Mössbauer effect, optical absorption etc., can also be obtained by the pseudomolecular model. In the present work, even though results for practical models have not been computed, the Debye-Waller factor of one of the nearest neighbours of a vacancy in the simple cubic lattice has been given in terms of the parameters of the lattice.

The theory of pseudomolecular model for the substitutional point defects involving a change in the short-range forces in lattices with polarisable atoms has also been given. The possibility of application of such an approach to general point defects which may change the long-range Coulomb interactions has not been investigated in the present work. Such an extension may provide a very useful model for the colour centers in ionic crystals.

APPENDIX I

The block-diagonalised form of $\Delta(\omega)$ (eqn. 3.3) for a substitutional defect in the simple cubic lattice

$$
\left| \Delta(\omega) \right| = \left(\frac{m}{m'}\right)
\begin{array}{|ccccccc|}
A_1 & B_1 & C_1 & 0 & 0 & 0 & 0 \\
A_2 & B_2 & C_2 & 0 & 0 & 0 & 0 \\
A_3 & B_3 & C_3 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & D & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & D & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & E & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & E \\
\end{array}
$$

$$\underbrace{\qquad\qquad}_{3A_{1g}} \quad \underbrace{\ }_{F_u} \quad \underbrace{\qquad}_{B_{1g}} \quad \underbrace{\ }_{A_{2u}}$$

with

$$A_1 = \frac{\gamma_2}{m}(1-\delta)\,\omega^2 G(000,000)\left[\frac{\delta M}{\Delta\gamma_2} - \frac{M}{\gamma_2}\right] + \delta$$

$$A_2 = -2\frac{\Delta\gamma_2}{M}\,\omega^2 G(100,000)\left[\frac{\delta M}{\Delta\gamma_2} - \frac{M}{\gamma_2}\right]$$

$$A_3 = \sqrt{2}\left(\frac{\Delta\gamma_2}{M}\right)\omega^2 G(001,000)\left[\frac{\delta M}{\Delta\gamma_2} - \frac{M}{\gamma_2}\right]$$

$$B_1 = 2(1-\delta)\frac{\gamma_2}{M}\left[G(000,000) - G(100,000)\right]$$

$$B_2 = 1 - \frac{\Delta\gamma_2}{M}\left[4G(100,000) - G(100,\bar{1}00) - 2G(100,010) - G(000,000)\right]$$

$$B_3 = 2\sqrt{2}(1-\delta)\frac{\gamma_2}{M}\left[G(001,000) - G(010,00\bar{1})\right]$$

$$C_2 = 2\sqrt{2}\,\alpha(1-\delta)\,\frac{\gamma_2}{M}\left[G(010,000)-G(010,001)\right]$$

$$C_3 = 1 + \alpha(1-\delta)\,\frac{\gamma_2}{M}\left[2G(001,000)-G(000,000)-G(001,00\bar{1})\right]$$

$$D = 1 + \frac{\Delta\gamma_2}{M}\left[G(000,000)-G(100,\bar{1}00)\right]$$

$$E = 1 - \frac{\Delta\gamma_2}{M}\left[2G(100,010)-G(100,\bar{1}00)-G(000,000)\right]$$

$$F = 1 + \alpha\,\frac{\Delta\gamma_2}{M}\left[G(000,000)-G(001,00\bar{1})\right]$$

where

γ_1 and γ_2 are the central and non-central nearest neighbour force constants ($\frac{\gamma_1}{\gamma_2}=\alpha$)

$$\delta = \frac{\gamma_2 + \Delta\gamma_2}{\gamma_2}\,,$$

m = mass of a normal atom,

$m+\delta m$ and $\gamma + \Delta\gamma$ are the mass and force constant of the substitutional impurity.

and

A_{1g}, E_u, B_{1g} and A_{2u} are the irreducible representations of the point symmetry group D_{4h}.

APPENDIX II

$\hat{G}_C(\omega)$ for the Isotropic Square Lattice (§3.4a)

$$
\hat{G}_C(\omega) = \begin{matrix} & 0 & 1 & 2 & 3 & 4 \\ 0 & g(0,0;\omega) & g(1,0;\omega) & g(1,0;\omega) & g(1,0;\omega) & g(1,0;\omega) \\ 1 & g(1,0;\omega) & g(0,0;\omega) & g(1,1;\omega) & g(2,0;\omega) & g(1,1;\omega) \\ 2 & g(1,0;\omega) & g(1,1;\omega) & g(0,0;\omega) & g(1,1;\omega) & g(2,0;\omega) \\ 3 & g(1,0;\omega) & g(1,0;\omega) & g(1,1;\omega) & g(0,0;\omega) & g(1,1;\omega) \\ 4 & g(1,0;\omega) & g(1,1;\omega) & g(2,0;\omega) & g(1,1;\omega) & g(0,0;\omega) \end{matrix}
$$

where

$$G_C(0,0) = G_C(1,1) = G_C(2,2) = G_C(4,4) = g(0,0;\omega);$$

$$G_C(1,0) = G_C(0,1) = G_C(2,0) = G_C(0,2) = G_C(3,0)$$
$$= G_C(0,3) = G_C(4,0) = G_C(0,4) = g(1,0;\omega);$$

$$G_C(2,1) = G_C(1,2) = G_C(2,3) = G_C(3,2) = G_C(3,4)$$
$$= G_C(4,3) = G_C(1,4) = G_C(4,1) = g(1,1;\omega);$$

and

$$G_C(1,3) = G_C(3,1) = G_C(2,4) = G_C(4,2) \equiv g(2,0;\omega).$$

APPENDIX III

Matrices $\hat{S}$ and $\hat{V}$ for the isotropic square lattice (§3.4a)

$$
\hat{S} \;=\;
\begin{array}{c|ccccc}
 & 0 & 1 & 2 & 3 & 4 \\
\hline
0 & 1 & 0 & 0 & 0 & 0 \\
1 & 0 & 1/2 & 1/2 & 1/\sqrt{2} & 0 \\
2 & 0 & 1/2 & -1/2 & 0 & 1/\sqrt{2} \\
3 & 0 & 1/2 & 1/2 & -1/\sqrt{2} & 0 \\
4 & 0 & 1/2 & -1/2 & 0 & -1/\sqrt{2}
\end{array}
$$

$$
\hat{V} \;=\;
\begin{array}{c|ccccc}
 & 0 & 1 & 2 & 3 & 4 \\
\hline
0 & 1/\sqrt{5} & -4/20 & 0 & 0 & 0 \\
1 & 1/\sqrt{5} & 1/20 & 1/2 & 1/\sqrt{2} & 0 \\
2 & 1/\sqrt{5} & 1/20 & -1/2 & 0 & 1/\sqrt{2} \\
3 & 1/\sqrt{5} & 1/20 & 1/2 & -1/\sqrt{2} & 0 \\
4 & 1/\sqrt{5} & 1/20 & -1/2 & 0 & -1/\sqrt{2}
\end{array}
$$

APPENDIX IV

$\hat{V}$ and $\hat{C}$ for the isotropic simple cubic lattice ($\S 3.4b$)

$$
\hat{V} = \begin{array}{c} \\ 0 \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array}
\begin{array}{ccccccc}
0 & 1 & 2 & 3 & 4 & 5 & 6 \\
1/\sqrt{7} & 6/\sqrt{42} & 0 & 0 & 0 & 0 & 0 \\
1/\sqrt{7} & -1/\sqrt{42} & 1/\sqrt{2} & 0 & 0 & 1/\sqrt{12} & 1/2 \\
1/\sqrt{7} & -1/\sqrt{42} & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{12} & -1/2 \\
1/\sqrt{7} & -1/\sqrt{42} & 0 & 0 & 1/\sqrt{2} & -2/\sqrt{12} & 0 \\
1/\sqrt{7} & -1/\sqrt{42} & -1/\sqrt{2} & 0 & 0 & 1/\sqrt{12} & 1/2 \\
1/\sqrt{7} & -1/\sqrt{42} & 0 & -1/\sqrt{2} & 0 & 1/\sqrt{12} & -1/2 \\
1/\sqrt{7} & -1/\sqrt{42} & 0 & 0 & -1/\sqrt{2} & -2/\sqrt{12} & 0
\end{array}
$$

$$
\hat{C} = \begin{pmatrix}
6\gamma & -\gamma & -\gamma & -\gamma & -\gamma & -\gamma & -\gamma \\
-\gamma & 6\gamma & 0 & 0 & 0 & 0 & 0 \\
-\gamma & 0 & 6\gamma & 0 & 0 & 0 & 0 \\
-\gamma & 0 & 0 & 6\gamma & 0 & 0 & 0 \\
-\gamma & 0 & 0 & 0 & 6\gamma & 0 & 0 \\
-\gamma & 0 & 0 & 0 & 0 & 6\gamma & 0 \\
-\gamma & 0 & 0 & 0 & 0 & 0 & 6\gamma
\end{pmatrix}
$$

$$\hat{v}^{+}\hat{G}_c\hat{v} = \begin{pmatrix} \frac{1}{7}(7g_0+12g_1 & \frac{\sqrt{6}}{7}(g_2+4g_3 & 0 & 0 & 0 & 0 \\ \quad +4g_3+g_2) & \quad -5g_1) & & & & \\ \frac{\sqrt{6}}{7}(g_2+4g_3 & \frac{1}{7}(7g_0+g_2 & 0 & 0 & 0 & 0 \\ \quad -5g_1) & \quad +4g_3-12g_1) & & & & \\ 0 & 0 & (g_0-g_2) & 0 & 0 & 0 \\ 0 & 0 & 0 & (g_0-g_2) & 0 & 0 \\ 0 & 0 & 0 & 0 & (g_0-g_2) & 0 \\ 0 & 0 & 0 & 0 & 0 & (g_0+g_2 \\ & & & & & \quad -2g_3) \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{matrix} \\ \\ \\ \\ \\ \\ \\ (g_0 \\ -2g_3 \end{matrix}$$

$$\hat{B}^{T}\hat{A}^{-1}\hat{B} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & P & Q & Q & R & Q & Q \\ 0 & Q & P & Q & Q & R & Q \\ 0 & Q & Q & P & Q & Q & R \\ 0 & R & Q & Q & P & Q & Q \\ 0 & Q & R & Q & Q & P & Q \\ 0 & Q & Q & R & Q & Q & P \end{pmatrix}$$

where

$$P = 6\gamma - \left\{ \frac{\gamma}{6} + \frac{1}{2}(g_0-g_2)^{-1} + \frac{1}{3}(g_0+g_2-2g_3)^{-1} \right\},$$

$$Q = \frac{\gamma}{6} - \frac{1}{6}(g_0+g_2-2g_3),$$

and $\quad R = \frac{\gamma}{6} - \frac{1}{2}(g_0-g_2)^{-1} + \frac{1}{3}(g_0+g_2-2g_3)^{-1}.$

APPENDIX V

V MATRIX FOR THE B.C.C. LATTICE

$$\tilde{v} = \begin{pmatrix} \hat{v}_{11} & \hat{v}_{12} & \hat{v}_{13} \\ \hat{v}_{21} & \hat{v}_{22} & \hat{v}_{23} \\ \hat{v}_{31} & \hat{v}_{32} & \hat{v}_{33} \end{pmatrix}$$

with

$$\hat{v}_{11} = \begin{pmatrix}
1/\sqrt{9} & -8/\sqrt{72} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 & 0 & 0 & 1/4 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4 & 0 & 0 & -1/4 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 & 0 & 0 & -1/4 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4 & 0 & 0 & 1/4 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 & 0 & 0 & 1/4 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4 & 0 & 0 & -1/4 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 & 0 & 0 & -1/4 \\
1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4 & 0 & 0 & 1/4
\end{pmatrix}$$

$$\hat{v}_{21} = \begin{pmatrix}
0 & 0 & 0 & 1/\sqrt{9} & -8/\sqrt{72} & 0 & 0 & 0 & 0 \\
0 & 0 & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 \\
0 & 0 & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 \\
0 & 0 & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4 \\
0 & 0 & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4 \\
0 & 0 & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 \\
0 & 0 & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & 1/4 \\
0 & 0 & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4 \\
0 & 0 & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & 0 & 0 & 0 & -1/4
\end{pmatrix}$$

$$\hat{V}_{31} = \begin{pmatrix}
O & O & O & O & O & O & 1/\sqrt{9} & -8/\sqrt{72} & O \\
O & O & 1/4 & O & O & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O \\
O & O & -1/4 & O & O & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O \\
O & O & -1/4 & O & O & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O \\
O & O & 1/4 & O & O & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O \\
O & O & 1/4 & O & O & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O \\
O & O & -1/4 & O & O & 1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O \\
O & O & -1/4 & O & O & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O \\
O & O & 1/4 & O & O & -1/4 & 1/\sqrt{9} & 1/\sqrt{72} & O
\end{pmatrix}$$

and the submatrices $\hat{V}_{12}$, $\hat{V}_{13}$, $\hat{V}_{22}$, $\hat{V}_{23}$, $\hat{V}_{32}$ and $\hat{V}_{33}$ are the same as those defined in Reference (31).

$$\hat{\Phi}_{22}^{s'} - \hat{\Phi}_{22}^{s} \quad (\S\,5.3):$$

Core–core

	(000)	(100)	(010)	(001)	($\bar1$00)	(0$\bar1$0)	(00$\bar1$)
(000)	$6(\Delta d+\Delta F)+\Delta K$	$-\Delta d$	$-\Delta d$	$-\Delta d$	$-\Delta d$	$-\Delta d$	$-\Delta d$
(100)	$-\Delta d$	$\Delta d+\Delta F$					
(010)	$-\Delta d$						
(001)	$-\Delta d$						
($\bar1$00)	$-\Delta d$						
(0$\bar1$0)	$-\Delta d$						
(00$\bar1$)	$-\Delta d$						

Shell–core

Core–shell

	(000)	(100)	(010)	(001)	($\bar1$00)	(0$\bar1$0)	(00$\bar1$)
(000)	$6(\Delta N+\Delta F)+\Delta K$	$-\Delta N$	$-\Delta N$	$-\Delta N$	$-\Delta N$	$-\Delta N$	$-\Delta$
(100)	$-\Delta K$	$\Delta N+\Delta F$					
(010)	$-\Delta F$	$-\Delta N$					
(001)	$-\Delta F$	$-\Delta N$					
($\bar1$00)	$-\Delta F$	$-\Delta N$					
(0$\bar1$0)	$-\Delta F$	$-\Delta N$					
(00$\bar1$)	$-\Delta F$	$-\Delta N$					

Shell–shell

Nearest-neighbour force constants between

(1) shell–shell = N (2) Core–core. = d (3) Core and shell of the same atom = K

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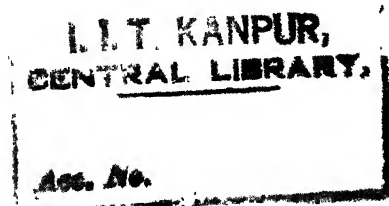
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